Monographs on Industrial Chemistry

COLOUR IN RELATION TO CHEMICAL CONSTITUTION

E. R. WATSON

MONOGRAPHS ON INDUSTRIAL CHEMISTRY

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INTRODUCTION

DURING the last four or five decades the Applications of Chemistry have experienced an extraordinary development, and there is scarcely an industry that has not benefited, directly or indirectly, from this expansion. Indeed, the Science trenches in greater or less degree upon all departments of human activity. Practically every division of Natural Science has now been linked up with it in the common service of mankind. So ceaseless and rapid is this expansion that the recondite knowledge of one generation becomes a part of the technology of the next. Thus the conceptions of chemical dynamics of one decade become translated into the current practice of its successor; the doctrines concerning chemical structure and constitution of one period form the basis of large-scale synthetical processes of another; an obscure phenomenon like Catalysis is found to be capable of widespread application in manufacturing operations of the most diverse character.

This series of Monographs will afford illustrations of these and similar facts, and incidentally indicate their bearing on the trend of industrial chemistry in the near future. They will serve to show how fundamental and essential is the relation of principle to practice. They

will afford examples of the application of recent knowledge to modern manufacturing procedure. As regards their scope, it should be stated the books are not intended to cover the whole ground of the technology of the matters to which they relate. They are not concerned with the technical *minutiæ* of manufacture except in so far as these may be necessary to elucidate some point of principle. In some cases, where the subjects touch the actual frontiers of progress, knowledge is so very recent and its application so very tentative that both are almost certain to experience profound modification sooner or later. This, of course, is inevitable. But even so, such books have more than an ephemeral interest. They are valuable as indicating new and only partially occupied territory; and as illustrating the vast potentiality of fruitful conceptions and the worth of general principles which have shown themselves capable of useful service.

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BY

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INDIAN EDUCATIONAL SERVICE; PROFESSOR OF CHEMISTRY, DACCA COLLEGE, BENGAL; TEMPORARY RESEARCH CHEMIST WITH BRITISH DYES, LTD.

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PREFACE

THIS volume is to some extent based on a course of lectures on "Colour and Constitution," which the author delivered at the University of Leeds in the May Term of 1917. Its preparation did not seem superfluous, as there was no monograph on the subject in the English language. A section of Smiles' *Chemical Constitution and Physical Properties*, part of Baly's article on "Spectrum Analysis," in the 1912–13 edition of Thorpe's *Dictionary of Applied Chemistry*, and some chapters of Cohen's *Organic Chemistry*, were the only summaries in our language, although the subject has received perhaps more attention in this country than in any other. In German there was Kayser's exhaustive treatise on *Spectroscopy*, of which the third volume gave an account of "Absorption Spectroscopy" up to 1905; and Ley's *Beziehungen zwischen Farbe und Konstitution* brought the account of the subject up to date in 1911.

In the present volume no attempt has been made to describe, or even refer to, every research bearing on the subject; but the author has tried to give a connected and simple account of the main lines on which research and discussion have taken place with regard to the relation between colour and chemical constitution, and the main theories which have been proposed as to the nature of the vibrations to which ordinary colour is due.

The early theories as to the relation between colour and constitution, such as the quinonoid theory and Nietzki's rule, have proved of great value for practical purposes, viz. in the production of dyestuffs and especially for the preparation of dyestuffs of any required shade; but more recent researches have shown that these classical theories are by no means

adequate. Modified and new theories have been proposed which agree better with the known facts.

The quest for the ultimate cause of colour has revealed the great complexity of the problem and has shown the need for further work in this direction. Both its scientific interest and its practical utility justify the most active prosecution of research in this field.

The thanks of the author are due to the Council of the Chemical Society, and to the writers of various papers in the Society's Transactions and elsewhere for permission to reproduce diagrams of absorption spectra, etc.

THE UNIVERSITY,
LEEDS,
28*th February*, 1918.

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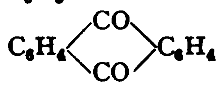
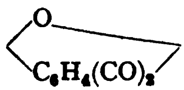
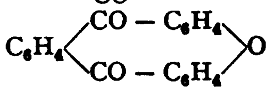
CHAPTER I

EARLY HISTORY OF THE SUBJECT

THE discovery of organic dye-stuffs may be said to have begun in 1856 by Sir W. H. Perkin's production of mauve. Before this time some natural dyes were known, together with a few artificial ones, *e.g.* picric acid and rosolic acid. But little was known as to their constitution. The discovery of mauve was rapidly followed by the production of a large number of new dyes and the investigation of their chemical constitution. It was only when some progress had been made in this direction that it became possible to study the relation between the colour and constitution of organic substances. The first recorded observation on the subject was made by Graebe and Liebermann in 1868 (*Ber. 1*, 106). These chemists pointed out that all the known coloured organic substances became colourless on the addition of hydrogen and arrived at the conclusion that their colour was due to some kind of close internal linking connected with oxygen and nitrogen atoms (double bonds between nitrogen atoms or between nitrogen and carbon, nitrogen and oxygen, or oxygen and carbon atoms) as, for example, in quinone and quinone derivatives, azobenzene, rosolic acid, and rosaniline.

The next recorded observation on the subject was made by O. N. Witt in 1876 (*Ber. 9*, 522) who brought forward his theory of *chromophores* and *auxochromes*. The nomenclature

of this theory is still largely used and the theory itself also is still recognised as a valuable if somewhat superficial relation between colour and constitution. Witt pointed out that two things are required to give an organic substance colour and dyeing properties. The molecule must possess a certain grouping of atoms to give it the potentiality for colour, and it must also possess a salt-forming radicle to bring out the colour and dyeing properties. The atomic groupings giving the potentiality of colour he termed *chromophores*, and molecules containing them were called *chromogens*. He specified the following chromophores and gave illustrations of chromogens containing them :—

Chromophores	*Chromogens*
NO_2	$C_6H_5NO_2$
$-N=N-$	$C_6H_5-N=N-C_6H_5$
$-CO-$	
	

It will be noticed that some of the chromogens are colourless, *e.g.* nitrobenzene and phenolphthaleïn, whilst others have a feeble colour, *e.g.* azobenzene and anthraquinone; but none of the chromogens has any dyeing property. The colour is developed or strengthened by the introduction of salt-forming radicles into the chromogens. These radicles he therefore termed *auxochromes*. Hydroxyl, amino- and substituted amino-groups, *e.g.* $NHCH_3$, $N(CH_3)_2$, etc., are the principal auxochromes. Not all salt-forming groups can act as auxochromes, *e.g.* sulphonic and carboxyl groups are without this function. The following table shows how the chromogens already mentioned are converted into dyes by the introduction of auxochromes—

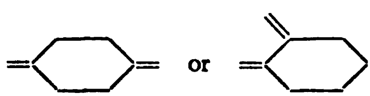
Chromogen	*Dye*	
$C_6H_5NO_2$	$C_6H_4(NO_2)OH$	Nitrophenol.
	$C_6H_4(NO_2)NH_2$	Nitraniline.

Chromogen	*Dye*
$C_6H_5-N=N-C_6H_5$	$C_6H_5-N=N-C_6H_4OH$ Benzene-azo-phenol.
	$C_6H_5-N=N-C_6H_4NH_2$ Aniline yellow.

Fluoresceïn.

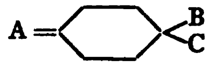
At the present time it may still be said that all dye-stuffs contain auxochromes, and if the list of chromogens is somewhat extended it may also be said that they all contain chromophores. But even in Witt's original communication there was some confusion between two distinct properties, viz. colour and dyeing properties; and whilst auxochromes were absolutely necessary for the development of dyeing properties, that was not the case with regard to colour, as some of the chromogens were themselves slightly coloured. We now know organic substances, *e.g.* nitrosobenzene, tertiary nitrosobutane and fulvene, which are intensely coloured, yet contain no auxochromes.

In a very unpretentious communication in 1888 (*Proc. Chem. Soc.*, 1888, pp. 27–33), H. E. Armstrong formulated the best-known theory which has ever been put forward as to the relation between the colour and constitution of organic compounds, viz. the *quinonoid* theory. He did not claim any particular novelty for his observations, but pointed out that the chemical formulæ of the well-known dye-stuffs either contained the *quinonoid* grouping or could be slightly modified or rearranged, in accordance with accepted ideas on tautomerism, so as to contain this grouping. The *quinonoid* grouping may be defined as a benzene nucleus to which other atoms or groups are attached by double bonds in the *para-* or *ortho-*positions.

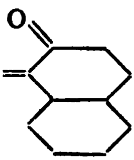


[It should be noted that in the true quinonoid arrangement the two external bonds from each of the *para-* or *ortho-*carbon

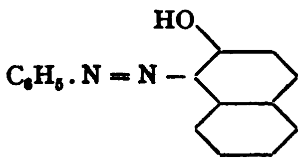
atoms must be attached to a single atom forming a typical double bond. The term *hemiquinoid* arrangement has been given for the grouping in which the two bonds from one of these nuclear carbon atoms are attached to different atoms, thus—



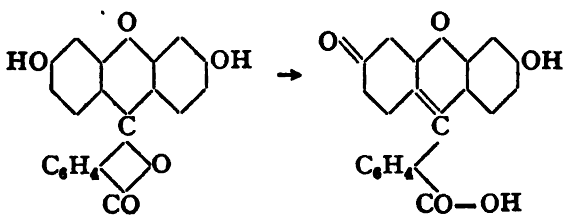
But it has never been suggested, except in a very tentative fashion, that the hemiquinonoid arrangement is sufficient to produce colour development.]

Armstrong and other chemists at that time were probably much impressed by the recently discovered fact that benzene-azo-β-naphthol was identical with the phenyl-hydrazone of β-naphthoquinone, so that there was as much justification for the formula $C_6H_5NH - N =$  as for the more

usual one based on the formation of the substance from β-naphthol and a benzene-diazonium salt, viz.—



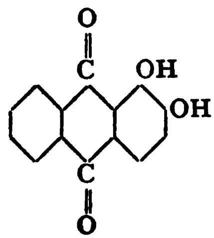
And if it were allowable to assume tautomerism to a quinonoid form in this case it might be allowable in other cases, *e.g.* in the case of fluoresceïn—



whilst in the case of *p*-rosaniline it was quite consistent with experimental facts to suppose that on the conversion of the base into salts there was elimination of a molecule of water and formation of a substance with a quinonoid structure—

$$HO.C\left\langle\begin{array}{l}C_6H_4.NH_2\\C_6H_4.NH_2\\C_6H_4.NH_2\end{array}\right. \xrightarrow{HCl} C\left\langle\begin{array}{l}C_6H_4=NH.HCl\\C_6H_4.NH_2\\C_6H_4.NH_2\end{array}\right. + H_2O$$

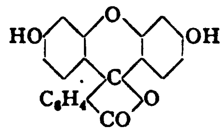
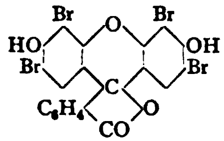
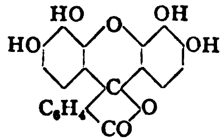
In many cases the ordinary formula already contained the quinonoid structure, as *e.g.* in the anthraquinone group.



Simultaneously with the publication of these views as to the cause of colour Nietzki formulated a rule (*Verhandl. des Vereins zum Beförderung des Gewerbefleisses*, 1879, *58*, 231) on the relation between constitution and *depth* of colour. [It should be carefully noted that the term *depth* is used by colour chemists in a very definite and limited way. In ordinary language the term depth of colour has at least two meanings. Blue and red are said to be deeper colours than yellow, and also one yellow is said to be deeper than another yellow if it is stronger or more intense, *i. e.* less admixed with white. Colour chemists restrict the use of the term and employ it for the first purpose only. Blue is deeper than red or yellow and red is deeper than yellow. The ordinary colours arranged according to depth are: green, blue, violet, red, orange, yellow, *i. e.* the complements to the ordinary colours of the spectrum taken in order from the red to the violet end.] It had been noticed that by methylating, ethylating, or phenylating rosaniline the colour was deepened; that the depth of colour attained was more or less proportional to the number of alkyl or aryl

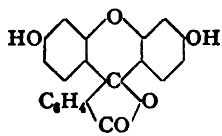
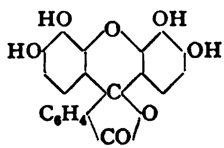
groups introduced; and that ethyl groups were more effective in this respect than methyl, and phenyl more effective than either. Nietzki formulated the general rule that the colour of a dye-stuff can be deepened by adding groups so as to increase its molecular weight and that the deepening of colour produced is more or less proportional to the increase of molecular weight. The following table shows that the rule holds in the triphenylmethane series and in other groups to a certain extent—

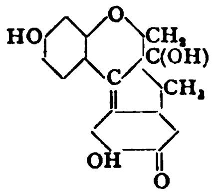
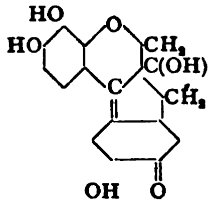
Name	Molecular formula	Mol. wt.	Shade of dyeing
Pararosaniline	$C\begin{cases} C_6H_4NH_2 \\ C_6H_4NH_2 \\ C_6H_4 = NH_2Cl \end{cases}$	281·5	Magenta
Methyl Violet R	$C\begin{cases} C_6H_4NHCH_3 \\ C_6H_4NHCH_3 \\ C_6H_4 = NHCH_3Cl \end{cases}$	323·5	Reddish violet
Methyl Violet 3B	$C\begin{cases} C_6H_4 . N(CH_3)_2 \\ C_6H_4 . N(CH_3)_2 \\ C_6H_4 . = N(CH_3)_2Cl \end{cases}$	365·5	Violet
Rosaniline Blue	$C\begin{cases} C_6H_4NHC_6H_5 \\ C_6H_4 . NHC_6H_5 \\ C_6H_4 = NHC_6H_5 . Cl \end{cases}$	509·5	Blue
Iodine Green	$C\begin{cases} C_6H_4 . N(CH_3)_2 \\ C_6H_4N(CH_3)_2 + CH_3I \\ C_6H_4 = N(CH_3)_2I \end{cases}$	599	Green
Benzene-azo-phenol	$C_6H_5 - N = N - C_6H_4OH$	198	Yellow
Benzene-azo-naphthol	$C_6H_5 - N = N - C_{10}H_6OH(\beta)$	248	Red
Biebrich Scarlet	$SO_3H . C_6H_4 - N = N - C_6H_3(SO_3H) - N = N - C_{10}H_6 . OH(\beta)$	512	Red
Naphthol Black	$(SO_3H)_2C_{10}H_5 - N = N - C_{10}H_6 - N = N - C_{10}H_4\begin{cases} OH \\ (SO_3H)_2 \end{cases}$	772	Black
Alizarin	$C_6H_4\begin{array}{c} CO \\ CO \end{array}C_6H_2(OH)_2$	240	Red (on alum)
Alizarin Bordeaux	$(OH)_2C_6H_2\begin{array}{c} CO \\ CO \end{array}C_6H_2(OH)_2$	272	Bordeaux (on alum)
Alizarin Cyanine	$(OH)_2C_6H_2\begin{array}{c} CO \\ CO \end{array}C_6H(OH)_3$	288	Violet (on alum)

Name	Molecular formula	Mol. wt.	Shade of dyeing
Fluorescein .		332	Yellow
Eosin . .		648	Red
Gallein .		364	Violet to blue (according to mordant.)
Indigotin .	$C_{16}H_{10}N_2O_2$	262	Indigo blue
Ciba Blue BB (Tetrabrom-indigotin)	$C_{16}H_6N_2O_2Br_4$	578	Greenish blue

But it should be at once mentioned that there are many exceptions to Nietzki's rule. The example of eosin and galleïn shows that the chemical nature of the added groups may be more important than their mere weight, so far as their effect on the colour is concerned. In this case two hydroxyl groups deepen the colour much more than four bromine atoms, although their weight is very much less. The effect produced depends also very much on the positions of the added groups. This subject is further discussed in Chapter V.

In the last paragraph we have drawn attention to the great effect on the depth of colour produced by adding additional hydroxyl groups to fluoresceïn. To a certain extent this may be regarded as only a special case of Nietzki's rule. But it has long been recognised that additional auxochromes are especially effective in producing a deepening of colour, and this rule was applied in 1888 in the production of new dyes of the anthraquinone series. The rule is illustrated by examples in the following table.

Nam .	Molecular formula.	Shade of dyeing.
Alizarin . .	$C_6H_4\langle{CO \atop CO}\rangle C_6H_2(OH)_2$	Red (on alum)
Alizarin Bordeaux	$(OH)_2C_6H_2\langle{CO \atop CO}\rangle C_6H_2(OH)_2$	Bordeaux (on alum)
Alizarin Cyanine	$(OH)_2C_6H_2\langle{CO \atop CO}\rangle C_6H(OH)_2$	Violet (on alum)
Fluoresceïn .		Yellow
Galleïn . .		Violet to blue (according to mordant)
Aniline yellow .	$C_6H_4-N=N-C_6H_4NH_2$	Yellow
Chrysoidine .	$C_6H_4-N=N-C_6H_3(NH_2)_2$	Orange
Azoorseilline .	$C_6H_4-N=N-C_{10}H_5(SO_3H)OH$ $\vert$ $C_6H_4-N=N-C_{10}H_5(SO_3H)OH$	Brownish red
Congo Violet .	ditto (isomeric)	Violet
Congo Red .	$C_6H_4-N=N-C_{10}H_5(SO_3H)NH_2$ $\vert$ $C_6H_4-N=N-C_{10}H_5(SO_3H)NH_2$	Red
Naphthocyanine	$C_6H_4-N=N-C_{10}H_4(SO_3H)(OH)_2$ $\vert$ $C_6H_4-N=N-C_{10}H_4(SO_3H)(OH)_2$	Blue
Diamine Black, B	$C_6H_4-N=N-C_{10}H_4(SO_3H)(OH)NH_2$ $\vert$ $C_6H_4-N=N-C_{10}H_4(SO_3H)(OH)NH_2$	Black
Diamine Blue, BB	ditto (isomeric)	Blue

Name	Molecular formula	Shade of dyeing
Brasileïn . .		Red
Haemateïn .		Blue

Although these early theories of Witt and Armstrong have been shown to be no longer tenable, and Nietzki' rule and the rule that colour can be deepened by the multiplication of auxochromes are now known to be true only to a limited extent, and to have many exceptions, nevertheless it may be asserted that it is these theories and rules which have served as guides in the production of many of our most important dye-stuffs, and that they are still the working rules by which the colour chemist is chiefly guided in his search for new colouring matters. For practical purposes it is still felt that the presence of both a chromophore and an auxochrome is generally necessary to give a substance dyeing properties, and the presence of the quinonoid structure in the molecular formula of a substance would probably still be regarded as one of the best indications that it was likely to be interesting from the point of view of the colour chemist. Nietzki's rule proved a useful guide in the production of complex azo-dyes, and, as already mentioned, the rule that multiplication of auxochromes causes a deepening of colour was applied with very fruitful results in the case of the hydroxyanthraquinone dyes and also in the azo- and phthaleïn groups.

CHAPTER II

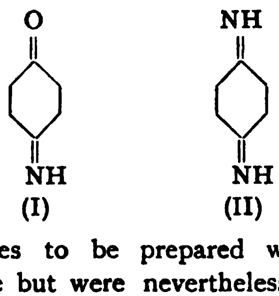
THE QUINONOID THEORY

Discussion of the Quinonoid Theory—Modifications of the Quinonoid Theory.

FEW theories have led to so much experimental work as the *quinonoid* theory of the cause of colour of organic compounds. This work has shown that the theory is untenable. On the one hand substances have been prepared which have a quinonoid structure but are colourless, and on the other hand coloured substances are known to which a quinonoid structure cannot be assigned.

Colourless Substances possessing a Quinonoid Structure

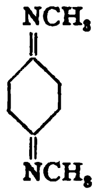
Iminoquinone (I) and di-iminoquinone (II) were perhaps



(I) (II)

the first substances to be prepared which possessed a quinonoid structure but were nevertheless colourless. The latter was prepared by Willstätter, Mayer, and Pfannenstiel (*Ber.* 1904, *37*, 1494) by the reduction of quinonedichlordiimine with hydrochloric acid in ethereal solution. Later, the mono- as well as the di-imino-compounds were obtained by oxidising *p*-aminophenol and *p*-phenylene diamine by shaking the ethereal solution with dry precipitated silver oxide and anhydrous sodium sulphate (*loc. cit.* 4605). By the same method of oxidation in an inert solvent with silver oxide

or lead peroxide Willstätter and his collaborators obtained quinone-dimethylimine (III) from *p*-dimethyl-phenylene-diamine, and diphenoquinone (IV) from *p*-dihydroxy-diphenyl,



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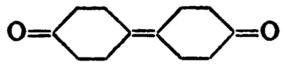


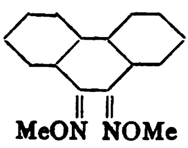
(IV)

The former is colourless in the crystalline form, though its solution is yellow; the latter crystallises in two modifications: one consisting of colourless needles whilst the other resembles chromic acid in appearance (*Ber.* 1905, *38*, 1232, 2244, 2348). Fuchsonimine (V) is colourless (Baeyer, *Zeit angew. chem.* 1906, *29*, 1287; *Ann. Rep. Chem. Soc.* 1906, 145)—

$$NH = C_6H_4 = C\begin{cases} C_6H_5 \\ C_6H_5 \end{cases}$$

(V)

and so also are the dimethyl ether (VI), the diacyl derivatives (VII) and the anhydride (VIII) of phenanthraquinone dioxime (J. Schmidt and J. Söll, *Jour. Chem. Soc. Abs.* 1907, i, 630, 1054)—



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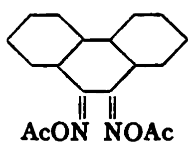
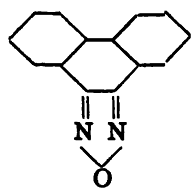


(VII)

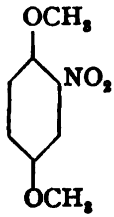


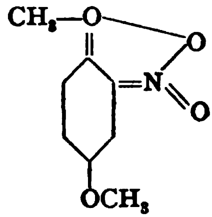
(VIII)

Coloured Substances to which a Quinonoid Structure cannot be assigned

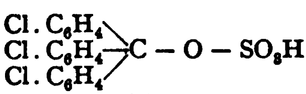
Nitroquinol dimethyl ether (I) is a substance about which there has been a good deal of discussion. It is obviously more difficult to prove that a substance is coloured than it is

to prove that one is colourless, as it can always be advanced in the way of argument that the apparent colour is due to traces of impurity. It is, however, said to have been shown that nitroquinol dimethyl ether is yellow when pure (H. Kauffmann, *Jour. Chem. Soc. Abs.* 1907, i, 127), and its molecular formula (I) does not contain the quinonoid structure. By the exercise of some ingenuity the formula may be rearranged so that it does contain this structure (II), but there seems no ground for assigning such a formula—


(I)


(II)

The sulphate of *p*-trichlortriphenyl carbinol (III) is highly coloured. (*Ber.*, 1905, *38*, 569, 1156.) It has been argued that a quinonoid structure (IV) or (V) can be assigned to this substance. But a substance with such a formula would be somewhat of the nature of an oxonium salt and would be expected to lose chlorine easily, whereas *p*-trichlortriphenyl carbinol sulphate does not react with silver nitrate solution (*loc. cit.*). The corresponding chloride does react in benzene solution with silver sulphate and more than one atom of chlorine is removed (Gomberg, *Jour. Chem. Soc. Abs.* 1907, i, 504), but an odour of quinone is observed at the same time (Baeyer, *ibid.* 691), which indicates that complete destruction of the molecule gradually takes place under these conditions.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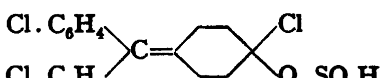
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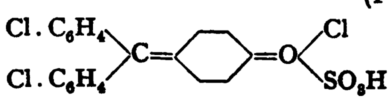
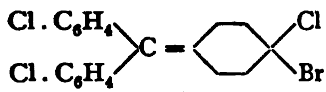

(V)

The point was further tested by a comparison of the ferrichlorides of tri-*p*-chlortriphenyl methyl bromide and tri-*p*-bromtriphenyl methyl chloride. By the action of water the organic part of the former loses only bromine and the latter only chlorine, whereas according to any quinonoid formula (VI) and (VII) both substances should behave in the same way.



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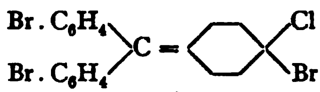
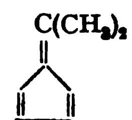


(VII)

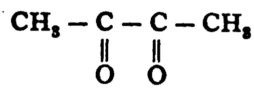
It may, moreover, be pointed out that formulæ IV, VI and VII are only hemiquinonoid and not quinonoid in the strict sense of the term.

The fulvenes, *e.g.* dimethyl fulvene (VIII), have a yellow colour, but cannot be assigned a quinonoid structure as some of them, *e.g.* dimethyl fulvene, do not even contain a benzene nucleus.



(VIII)

Some fatty compounds, *e.g.* diacetyl (IX), tertiary nitroso-compounds such as *tert.* nitrosobutane (X) and dinitro-



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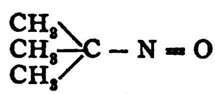


(X)

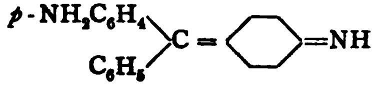
paraffins are coloured. Obviously their formulæ cannot contain the quinonoid structure as they do not contain the benzene nucleus.

Modifications of the Quinonoid Theory

Baeyer's Theory

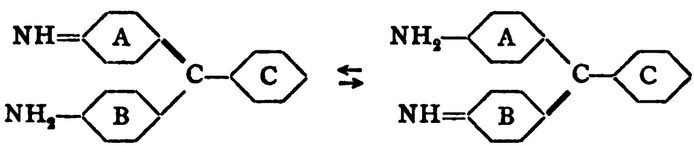
It has already been mentioned that fuchsonimine is colourless. The introduction of a *para*-amino-group into

one of the phenyl groups (I) causes the development of colour.

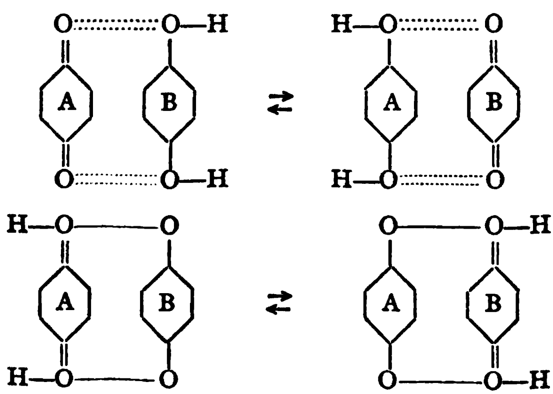


(I)

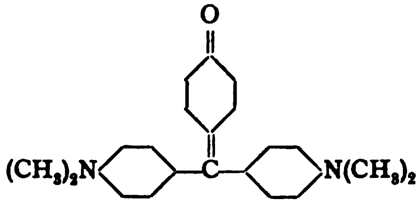
This and similar facts led A. v. Baeyer to suggest that the cause of colour is an oscillation of the quinonoid condition between two or more benzene nuclei (*Jour. Chem. Soc. Abs.* 1907, i, 504). If we call the three benzene nuclei in the above compound A, B, and C, it will be seen that the oscillation of a hydrogen atom will allow A and B alternately to become quinonoid.



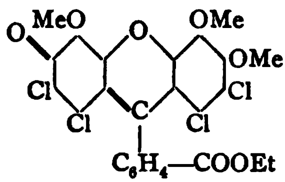
Baeyer suggested that this oscillation was the cause of the colour. A study of the quinhydrones led Willstätter to propose the same theory. (*Ber.*, 1908, *41*, 1458, 3245.) He suggested that the colour of the quinhydrones is due to an oscillation by which the two benzene nuclei become in turn quinonoid. This may be represented graphically in either of the following ways.



It was pointed out, however, that we can have colour development in the triphenylmethane series when such an oscillation is not possible—as in the case of *p*-tetramethyldiaminofuchsone. (Schlenk, *Ann.* 1909, *368*, 271, 277, 295.)



There are also known coloured quinhydrones in which such an oscillation is not possible, *e.g.* tetrachlor-*p*-benzoquinone forms strongly coloured quinhydrones with quinol dimethyl ether and with tetramethyl-*p*-phenylenediamine (Schlenk, *loc. cit.*) and there are other coloured substances in which such an oscillation is not possible, *e.g.* in the salts and esters of the trimethylether of tetrachlorgalleïn. (Orndorff and Delbridge, *Amer. Chem. J.* 1909, *42*, 183.)

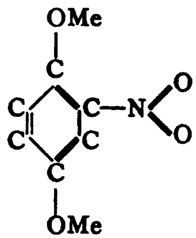


In fact, Baeyer and Willstätter can scarcely have meant to suggest that such an oscillation was the only cause of colour, as there are many coloured substances known which contain only one benzene nucleus, *e.g.* benzoquinone itself. Perhaps they meant to suggest that such an oscillation is necessary for the development of strong colour. All the arguments against the original quinonoid theory necessarily apply with still greater force against this modified quinonoid theory.

H. v. Liebig's Theory that $-\overset{\|}{A}-\overset{\|}{A}-\overset{\|}{A}-$ *is the Essential Organic Chromophore*

The fact that the fulvenes are coloured, although they do not contain the quinonoid structure, led H. v. Liebig to suggest

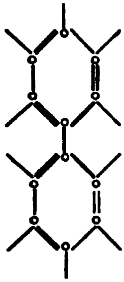
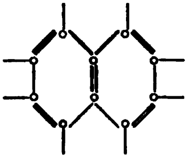
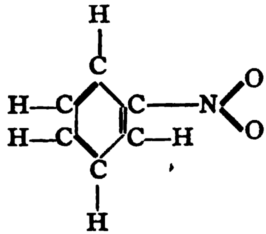
that the essential cause of colour is the arrangement of linkages which is possessed both by quinonoid compounds and the fulvenes, viz. $-\overset{\|}{A}-\overset{\|}{A}-\overset{\|}{A}-$ (*Ann.* 1908, *360*, 128). He added that this grouping is not, however, sufficient in itself to bring about colour. Some further condition, most frequently the closing of a ring, is necessary. The theory explains the colour of nitroquinol dimethyl ether which contains the postulated arrangement of linkages together with the ring—



By the same argument nitrobenzene should be coloured —but it is not. The colour of solutions of diacetyl is supposed to be due to polymerised molecules. The theory will not explain the colour of *tert.*-nitrosobutane. Bamberger (*Ber. 36*, 685) has studied the molecular weight of this substance in solutions. The blue solutions are unimolecular, whilst bimolecular solutions are colourless. Most of the arguments advanced against the quinonoid theory apply to this theory also.

Kauffmann's Auxochrome Theory

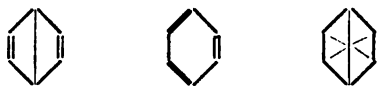
Whilst admitting that certain fatty compounds, *e.g.* the tertiary nitroso-compounds, may exhibit colour without containing the arrangement postulated by H. v. Liebig, H. Kauffmann has advanced reasons for believing that this arrangement is the essential cause of colour in ring compounds. (*Ueber den Zusammenhang Zwischen Farbe und Konstitution, Ahren's Vorträge*, 1904, pp. 45-50.) H. v. Liebig's theory has been criticised on the ground that some substances containing the arrangement $-\overset{\|}{A}-\overset{\|}{A}-\overset{\|}{A}-$ are colourless, *e.g.* diphenyl, naphthalene, and nitrobenzene.

Kauffmann's study of the behaviour of substances under the influence of the Tesla rays has led him to the conclusion that the substances above mentioned do not contain the arrangement of bonds as shown in the above formulæ, but that the introduction of certain groups—as, for example, azo-groups into benzidene and naphthalene or hydroxyl groups into nitrobenzene—rearranges the bonds in these molecules, so that they take up the positions here shown, whereupon colour is developed.

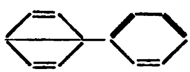
Kauffmann examined the behaviour of a large number of substances in the form of vapour under reduced pressure when subjected to the influence of Tesla rays (*Ber.* 1900, *33*, 1725; 1901, *34*, 682; 1902, *35*, 3668). He found they could be arranged in a series according to the extent to which they became luminous under the influence of these rays, and that those which became strongly luminous retained the property to some extent when the pressure was increased, or even when they were examined in the liquid or solid condition. The introduction of auxochromes into the benzene nucleus increased the luminescence, whilst carboxyl, nitro-, and azo-groups had the contrary effect. Thus benzene itself occupied a position midway between its various derivatives. Naphthalene responded to the Tesla rays more vigorously than benzene. Kauffmann also noticed that this property ran parallel with certain other physical and chemical properties. Those substances which became strongly luminous showed positive anomaly of magnetic rotation; those which did not respond at all to the Tesla rays showed negative anomaly, whilst

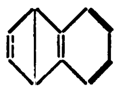
the intermediate substances had a normal value for the molecular magnetic rotation. Again, tendency to oxidise to quinoïd compounds is proportional to the strength of luminescence. Kauffmann came to the conclusion that the benzene nucleus is in different conditions in different compounds, that of the strongly luminous compounds being best represented by Dewar's formula (I), that of the non-luminous substances by the Claus diagonal formula (III), whilst the Kekulé formula (II) represented the condition of the intermediate compounds with moderate luminescence and normal magnetic rotation.



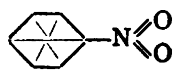
(I) (II) (III)

Now diphenyl and naphthalene both show considerable luminescence in the Tesla rays, so that at least one benzene nucleus in these compounds is in condition (I). Consequently the formulæ do not contain the arrangement which v. Liebig considers necessary for the development of colour—

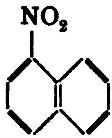
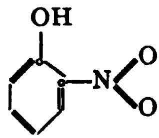




Nitrobenzene lies at the other end of the scale, and consequently it also does not contain the arrangement postulated by v. Liebig.



But if we add negative groups, such as NO_2, azo-group, carboxyl group, ketonic group, etc., to substances in condition (I), their luminosity is diminished and they assume condition (II). Similarly auxochromes, added to substances in condition (III), cause them also to assume the midway condition, so that, for example in nitronaphthalene and nitrophenol, we have the v. Liebig arrangement and consequently colour development.

Kauffmann's views on the cause of colour in ring compounds, as stated above, are generally referred to as his auxochrome theory, although they are essentially arguments in favour of H. v. Liebig's theory that the arrangement —A—A—A— is the essential organic chromophore.

In the opinion of the present writer Kauffmann's views and arguments are much weakened by the behaviour of methoxy- and ethoxy-groups.

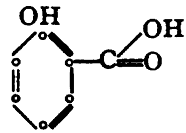
The alkylation of hydroxyl groups does not lessen the luminescence in the Tesla rays. On the contrary the effect is somewhat increased. The magneto-optical anomaly is also not lessened by alkylation.

	Magneto-optical Anomaly.
Resorcin	0·61
Pyrogallol	1·16
Pyrocatechin	1·35
Quinol dimethyl ether	3·00

But, as is well known, the alkylation of hydroxyl groups practically destroys their power as auxochromes—*e.g.* quercetin has a strong yellow colour, but its pentamethyl ether is colourless. It is true that in the presence of strong mineral acid methoxy- and ethoxy-groups have about the same auxochromic effect as the hydroxyl group; but under ordinary circumstances they can scarcely be regarded as auxochromes at all, whilst, according to Kauffmann's views, they should be just as good, or better, than hydroxyl groups.

Another argument against Kauffmann's view is the failure of hydroxyl groups to produce colour when introduced into benzoic acid. The carboxyl group is negative, and consequently in benzoic acid the benzene nucleus is in condition (III). The introduction of a hydroxyl group should throw it into condition (II), so that in hydroxybenzoic acid

we should have the arrangement which produces colour—according to H. v. Liebig's theory.



During the course of the above discussions it became evident to most chemists that it was unsatisfactory and dangerous to trust to eye observations alone in attempting to find out the cause of colour. Visible colour is due to selective absorption in the visible part of the spectrum: in other words, to absorption bands in the visible part of the spectrum; and it appeared more satisfactory to study the absorption bands themselves rather than one of the effects of their presence, viz. the physiological sensation of colour. We have already seen that there is some evidence for the theory that the colour of a substance can be deepened by weighting the molecule (Nietzki's rule)—in other words light waves of less frequency are absorbed by the molecule when it is weighted. Let us suppose for a moment that a certain grouping or arrangement in the molecule is the cause of absorption bands, which lie in the ultra-violet for substances of small molecular weight containing this arrangement, but are shifted into the visible spectrum by weighting the molecule. Investigations depending on eye observations would never be able to discover the cause of the colour, because it would be argued that the coloured heavier derivatives contained the arrangement causing colour, but the lighter parent substances did not, and thus the investigator would be put on the wrong track.

The point may be otherwise expressed by saying that visible colour is due to (1) absorption bands, (2) the fact that those absorption bands happen to be in the visible part of the spectrum; and any inquiry into the cause of visible colour

must concern itself with two points, viz. (1) the cause of the absorption bands, (2) the cause of those absorption bands being in the visible part of the spectrum. [From this point of view it is obvious that the arguments against the quinonoid theory are unsound which are based on the existence of colourless substances possessing a quinonoid structure.] A quotation on the subject from the Chemical Society's *Annual Report* for 1907 (p. 112) may be permitted because of its great importance: "It is now generally recognised that a more precise meaning must be given to the idea of colour than has often been the case. The production of physiological colour, due to the occurrence of absorption in the visible spectrum, is more or less an accidental circumstance. Absorption bands may occur in the ultra-violet of equal importance with those in the visible spectrum. In some cases a change in the frequency of the absorbed rays may cause a band to move from the ultra-violet into the visible region without any change of form. A colourless substance may, therefore, be converted into a coloured one without any real change in constitution having taken place, the alteration in the molecule being only of such a nature as to cause a certain retardation of those oscillations within it which give rise to the absorption. A study of the colour of a substance thus involves the examination of its entire visible and ultra-violet spectrum (the absorption bands in the infra-red appear to have a different origin, and may be neglected for the purpose of the present discussion), and further, as Hartley and his successors have shown, of the change of absorption with the concentration of the absorbing substance, the results being expressed in the form of curves. The quantitative study of the absorbing power of a substance, expressed in this manner, makes an exact comparison of different derivatives possible, and relationships are made evident which would escape notice if the examination were confined to visual observations of colour."

CHAPTER III

ABSORPTION SPECTRA—METHODS OF EXAMINING AND RECORDING

THE absorption spectrum of a liquid or solution can be obtained by passing white light through a layer of the liquid and then into the slit of a spectroscope. If the liquid is coloured probably one or more dark bands will be seen across the visible part of the spectrum; in some cases no definite bands are seen, but one end of the spectrum is darkened. If there is absorption in the ultra-violet a photograph of this part of the spectrum will show one or more dark bands or one end or the other may be cut off. Fig. 1 shows the general character of absorption bands. It is a photograph of the ultra-violet part of the spectrum of light which has passed through an ethereal solution of cotarnine. In this case the light was obtained from a metallic arc. The spectrum of this light is not continuous, but consists of a large number of fine lines. The top line shows the complete spectrum of the arc. In parts of the spectrum these fine lines are obliterated by the absorption bands of the cotarnine solution. This photograph brings out very clearly the great difference between absorption spectra and the spectra of metallic arcs and the light emitted from flames coloured by metallic salts or from gases under reduced pressure on the passage of an electric current. In the latter cases the spectrum consists of very sharp narrow bands, or lines, of which the positions can be determined very easily and accurately. Absorption bands are generally much broader and fainter, and it is a much more difficult matter to determine their positions exactly.

The earlier observers did their best to determine the positions of the centres of these bands, and the absorption

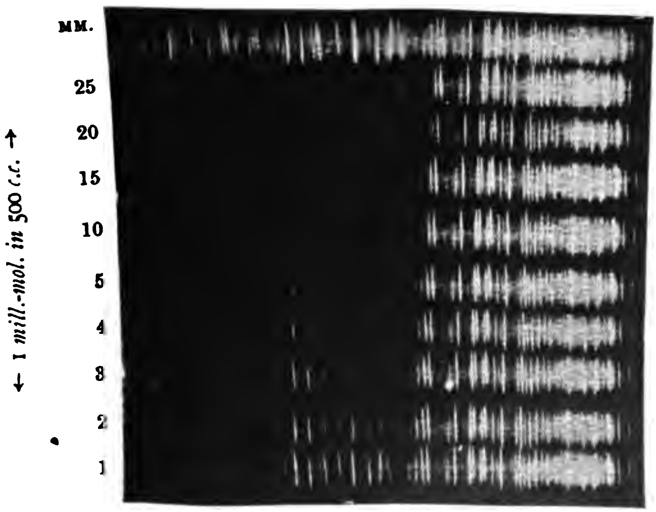


FIG. 1.—COTARNINE (IN ETHER).

(Reproduced from Dobbie's paper, *Chem. Soc. Trans.*, 1903, **83**, Plate I, opposite p. 604, lower figure.)

spectrum of a substance was recorded as containing bands in these positions, *e.g.* in Kayser's *Handbuch der Spectroscopie*, Vol. III, the absorption spectrum of galleïn in water is described as containing, according to Vogel (*Practische Spectralanalyse*, Berlin, 1889), a band between D and F, according to Formánek (*Spectralanalytischer Nachweis*, Berlin, 1900), two bands at 541 and 497 respectively. Sometimes the observations were recorded graphically by lines drawn

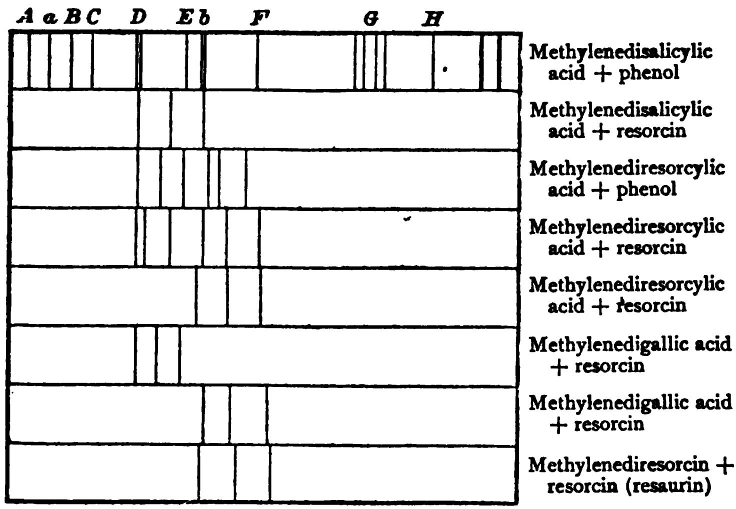


FIG. 2.

(Reproduced from Caro's paper, *Ber.* 1892, **25**, p. 2674.)

across the spectrum at the positions of the centres of the bands (Fig. 2).

It was soon recognised, however, that this was not a sufficient description of an absorption spectrum, as it gave no idea of the breadth of the bands, whilst, as a matter of fact, their breadth was one of their most characteristic features. Consequently some observers described absorption bands by recording the positions of their edges instead of their centres. They were graphically represented by black bands of the requisite width across the spectrum (Fig. 3).

This was also seen to be insufficient, as it was found that the breadth of the bands was different according as a thinner or thicker layer of liquid or solution was examined. Consequently some observers recorded the positions of the edges of the bands for thick layers and also for thin layers, and represented this graphically (Fig. 4).

It was also noticed that some bands had much sharper edges than others, and that one edge of a band might be much sharper than the other. Attempts were made to represent this graphically by shading the absorption bands

OXYHAEMOGLOBIN. HAEMOGLOBIN (reduced.)

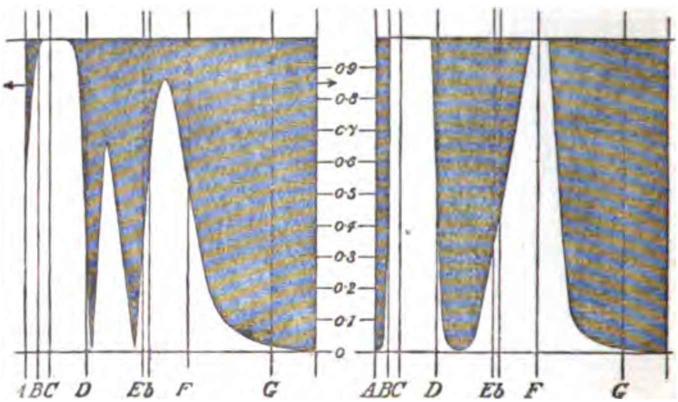


FIG. 4.

(From Allen's *Commercial Organic Analysis*, Messrs. J. and A. Churchill.)

making them darkest in the centre and lighter towards the edges. Formánek attempted to record graphically whether the two edges of the bands were equally sharp or which was the sharper.

Some observers published photographs of the absorption spectra; and in order to show in one photograph how the width of the bands varied with the thickness of the layer of liquid examined, the light was passed through the liquid contained in a wedge-shaped cell, so that the light passing into the top part of the slit of the spectroscope had passed through a thick layer of the liquid, whilst that passing into the bottom part of the slit had only traversed a thin layer. This made

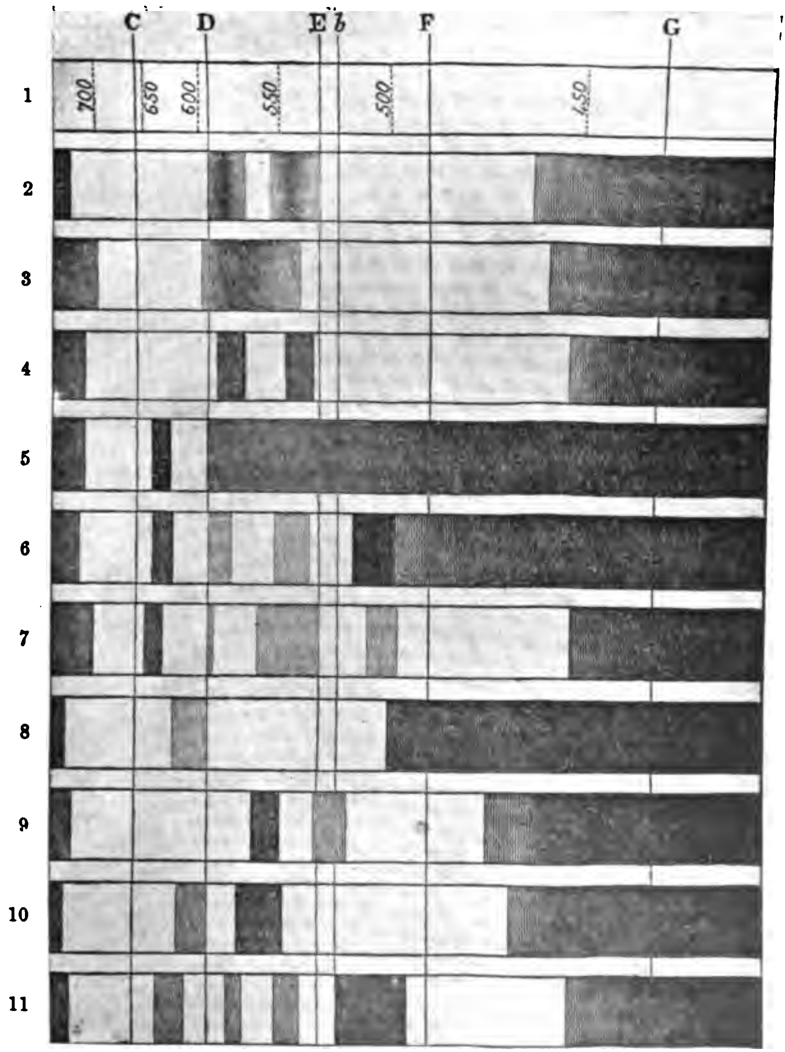


FIG. 3.—ABSORPTION SPECTRA OF BLOOD-COLOURING MATTERS.

2. Oxyhaemoglobin.
3 Haemoglobin.
4. Carbonyl-haemoglobin.
5. Methaemoglobin.
6. Methaemoglobin.
7. Acid haematin.
8. Alkaline haematin.
9. Haemochromogen.
10. Acid haematoporphyrin.
11. Alkaline haematoporphyrin.

(From Allen's *Commercial Organic Analysis*, Messrs. J. and A. Churchill.)

Naphthol yellow 1/1000 (*blue end only*).

Martius yellow 1/2500 (*blue end only*).

Filter yellow K 1/1000 (*blue end only*).

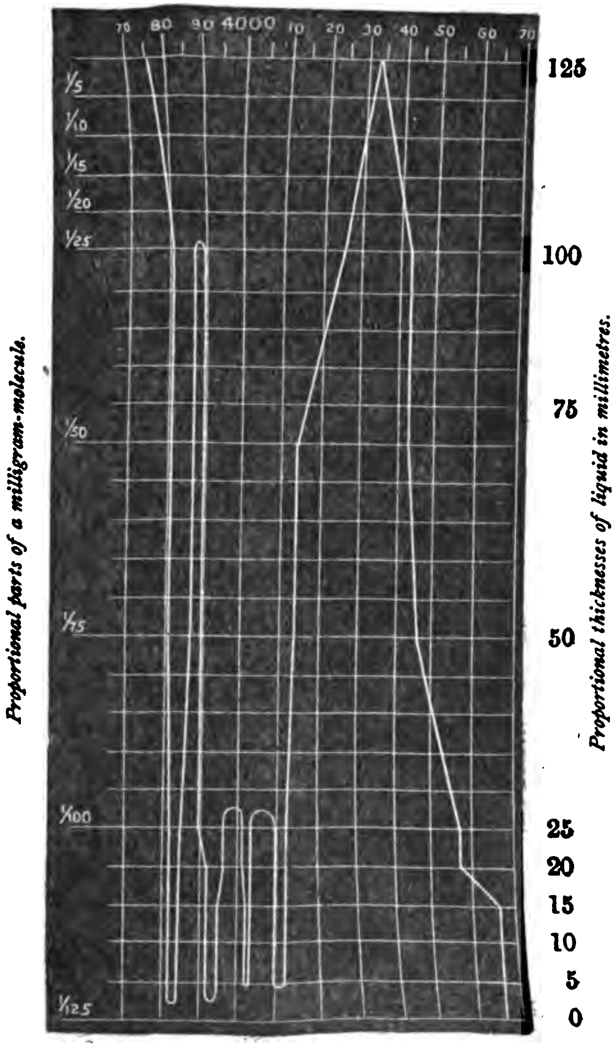
Aurophenine ammonia salt 1/1000 (*blue end only*).

FIG. 5.

(Reproduced from *An Atlas of Absorption Spectra*, by C. E. Kenneth Mees, D.Sc., of the Eastern Kodak Research Laboratory, Rochester, New York, p. 14, Figs. 5-8.)

the bands wider at the top than at the bottom of the spectrum (Fig. 5).

Scale of Oscillation-frequencies.



Curve of Molecular Vibrations—

FIG. 6.—BENZENE.

(Reproduced from Hartley's paper, *Chem. Soc. Trans*, 1885, 47, p. 747.)

In 1879 Hartley devised a method of representing by a single curve all the essential facts about the absorption spectrum of a liquid or of a substance in solution in a particular solvent. The positions of the edges of the absorption bands were determined for layers of different thicknesses, and plotted on a curve with wave-lengths or frequencies as abscissa and thickness of the layer as ordinate. The curve by which Hartley represented the absorption spectrum of

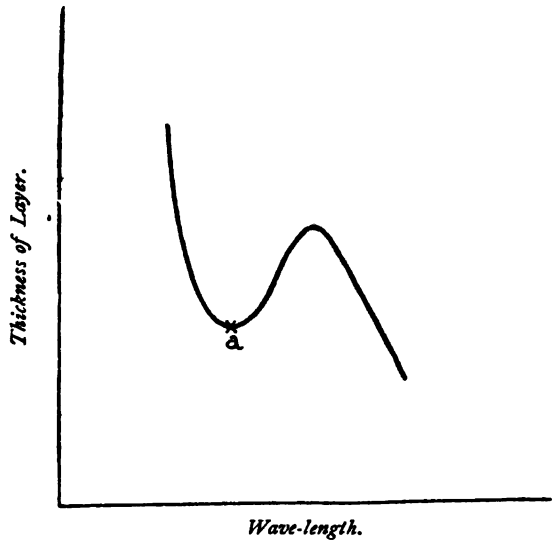


FIG. 7.

benzene is given in Fig. 6, and may be taken as a typical absorption curve.

These curves show at once the positions of the centres of the absorption bands and also the positions of the edges for layers of any thickness.

They also show at a glance whether the bands are symmetrical or not, and the minimum thickness of liquid necessary to show absorption. The point *a* (Fig. 7) is defined as the *head* of a band, and the ordinate of this point indicates the *persistence* of the band.

This method of recording the results of observations

in absorption spectra has been almost universally adopted, with one slight modification introduced by Hartley himself. It was found that in many cases the details of the curves could not be properly shown unless they were drawn on an inconveniently large scale—*e.g.* in Fig. 8, which gives the absorption curves for some dyes of the triphenylmethane series, most of the details of the curves are crowded at the bottom of the figure. This is obviated if instead of the thickness of the layers we give the logarithm of the thickness as ordinate. This has the effect of pulling out the curve in some places and contracting it in others; and it is found in practice that the essential features of the absorption curves of most substances are more clearly shown in this way than if the ordinate is directly proportional to the thickness of the layer. Fig. 36 shows the absorption curve of one of the triphenylmethane dyes drawn in this modified way.

In order to draw these curves it is necessary to determine the positions of the edges of the absorption bands for layers of different thickness. Baly has devised a simple apparatus by which the thickness of the layer of liquid under examination can be quickly changed (Fig. 9).

It consists of two tubes with optically worked plane ends, one tube being smaller than the other and sliding in it through a sleeve or collar of rubber-tubing. The common axis of the tubes is placed parallel to the beam of light which thus passes normally through the optically worked ends of the tubes and through the liquid between them. By sliding the narrower tube in or out the thickness of the layer of liquid between the two plane ends is made less or greater. A reservoir connected with the outer tube supplies more liquid or receives the surplus as the inner tube is pulled out or pushed in. A scale engraved on the outer tube enables the observer to read at once the thickness of the layer of liquid under examination. Instead of examining very thin or very thick layers of solution it is convenient to prepare several solutions of different concentrations, as the same effect can be obtained by a thin layer of a concentrated solution or a thicker layer of a more dilute one. According to Beer's Law, which experiment has

proved to be correct within a wide range, and which has also a theoretical basis, the thickness of layers must be inversely proportional to the concentration for the solutions to absorb

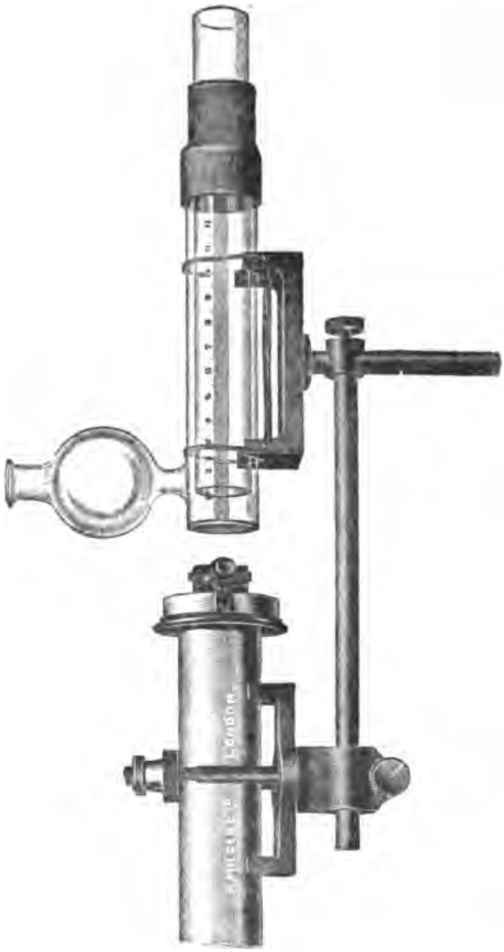


FIG. 9.
(Reproduced from Hilger's *Catalogue*, Section F, Fig. 5.)

light to the same extent. Thus, a layer 1 cm. thick of a normal solution will absorb as much light as a layer 2 cm. thick of a semi-normal solution, and so on.

The positions of the edges of an absorption band for any

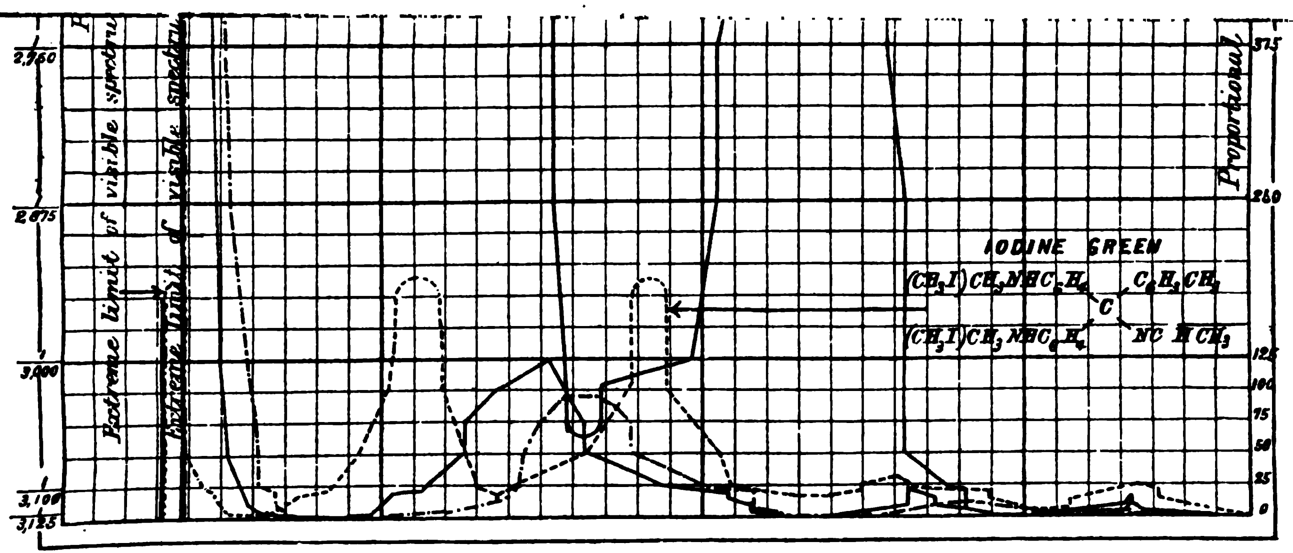


FIG. 8.
(Reproduced from Hartley's paper, *Chem. Soc. Trans.*, 1887, 51, Plate I.)

given thickness of liquid may be determined by eye-observation in the visible part of the spectrum or by photography either for the visible or the ultra-violet. In either case it is advisable to arrange to have the spectrum of the unabsorbed light thrown into the eye-piece or on to the screen directly above and contiguous to that of the light passed through the absorbing liquid. It is often convenient to use a metallic arc as a source of light. This gives a spectrum consisting of a large number of characteristic lines. In a photograph these lines become faint inside an absorption band, and the position of the first line to become perceptibly faint may be taken as that of the edge of the band.

But the edges of many absorption bands are very indefinite. The absorption is greatest in the centre of a band and becomes less and less as we proceed towards the edge. Theoretically the edge might be defined as the point where absorption entirely ceases, but in practice there will be a limit below which absorption cannot be detected. This makes the position of the edge somewhat indefinite. If it is being determined by eye-observation, a very sensitive eye will detect absorption sooner than a less sensitive one, and will record the band broader in consequence. The human eye varies in its sensitiveness, hence different observers will not always agree as to the position of the edge of a band, and the same observer will get different results from time to time. Again, a small difference cannot be so easily detected in a strong light as in light of more moderate intensity, so that somewhat different results will be obtained according to the intensity of the source of light. These difficulties are not altogether overcome by relying on photographs. The point at which the first sign of absorption can be detected in a photograph will depend on the intensity of the source of light, on the length of the exposure and on the extent to which development of the photograph is carried.

These difficulties are to a great extent overcome by the use of a spectrophotometer, and this instrument is coming more and more into use for the observation of absorption spectra. By the use of this instrument we obviate the difficult

task of deciding at what point absorption begins, and determine instead the points at which definite percentages (such as 5%, 10%, 15%, etc.) of the light are absorbed. This is achieved by

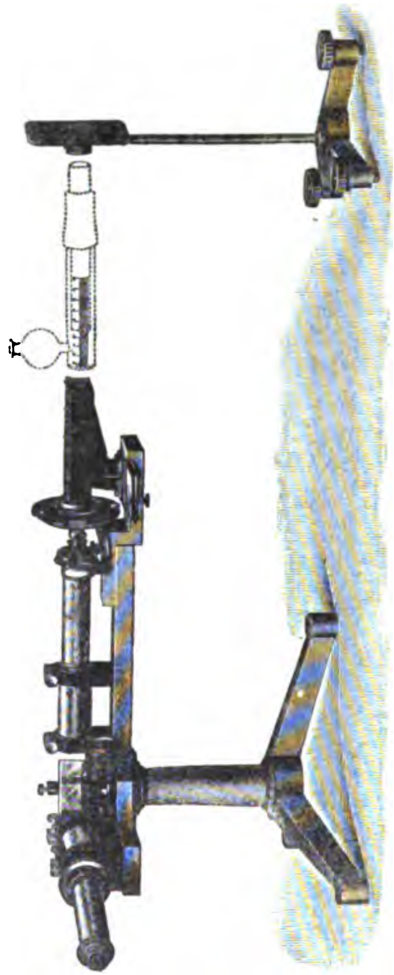


FIG. 10.
(Reproduced from Hilger's *Catalogue*, Section F, Fig. F 4.)

dividing the light into two beams, one of which passes through the absorbing medium and the other through some apparatus by which its intensity may be reduced by any desired fraction. Both beams eventually pass into the spectroscope and give

their spectra one above and contiguous to the other in the eye-piece or on the screen. It is then a fairly easy matter to determine the point at which the two spectra are of equal intensity.

For eye-observation in the visible part of the spectrum a very convenient apparatus is the Nutting Polarisation Photometer attachment, which is shown in use in Fig. 10.

In this apparatus the beam of light which does not pass

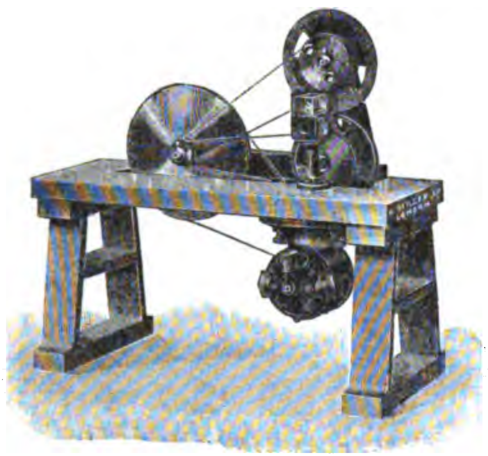


FIG. 11.

(Reproduced from Hilger's *Catalogue* [Spectrophotometers], Fig. 2.)

through the absorbing medium is reduced by any desired fraction by an arrangement of Nicol's prisms.

For photographic work in the ultra-violet the beam of light which does not pass through the absorbing medium is best reduced by passing through a rotating sector, the aperture of which can be varied (Fig. 11).

The observations with the spectrophotometer enable us to draw a curve for each concentration of solution, the wave-length being taken as the abscissa and the percentage of light absorbed as the ordinate. Such a curve is shown in Fig. 12.

These curves show at a glance how the intensity of absorp-

tion falls off at the edges of the bands and whether the bands are symmetrical or not.

It may be noted here that the spectrophotometer has a very great advantage over the ordinary spectroscope in the examination of solids and dyed fabrics. By the older method we can only record the positions of the edges of the absorption

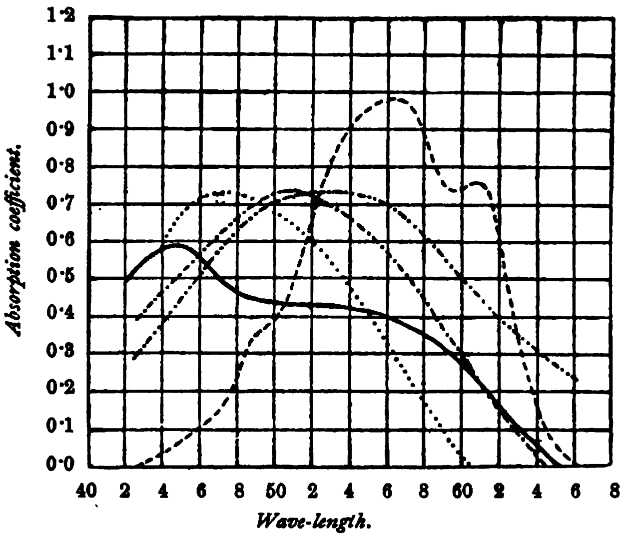


FIG. 12.

Alizarin or 1:2-dihydroxyanthraquinone.

——— Alizarin in alcohol, N/10⁴, 10 mm. thickness.
- - - - „ in KOH, N/10⁴, 10 mm. thickness, 400 mols. KOH.
. . . . . . „ on tin mordanted wool, ½ per cent. dyeing.
—·—·— „ on alum mordanted wool, ½ per cent. dyeing.
—··—··— „ on chrome mordanted wool, ½ per cent. dyeing.

(Reproduced from Meek and Watson's paper, *Chem. Soc. Trans.*, 1916, 109, p. 545, Fig. 1.)

bands in the light reflected from a solid, but no curve can be drawn from these isolated observations. But by the use of the spectrophotometer we can construct "wave-length—light absorbed" curves which can be directly compared with similar curves for solutions of the same substance or chemically related substances (Meek and Watson, *Jour. Chem. Soc. Trans.* 1916, *109*, 545–6).

It will be noticed that the curves obtained by the spectrophotometer are not the same as those obtained by the older method. In the former the ordinate is the percentage of light absorbed, in the latter it is the thickness of the layer examined. There is, however, an intimate connection between the two. If we examine layers of different thicknesses (or, what

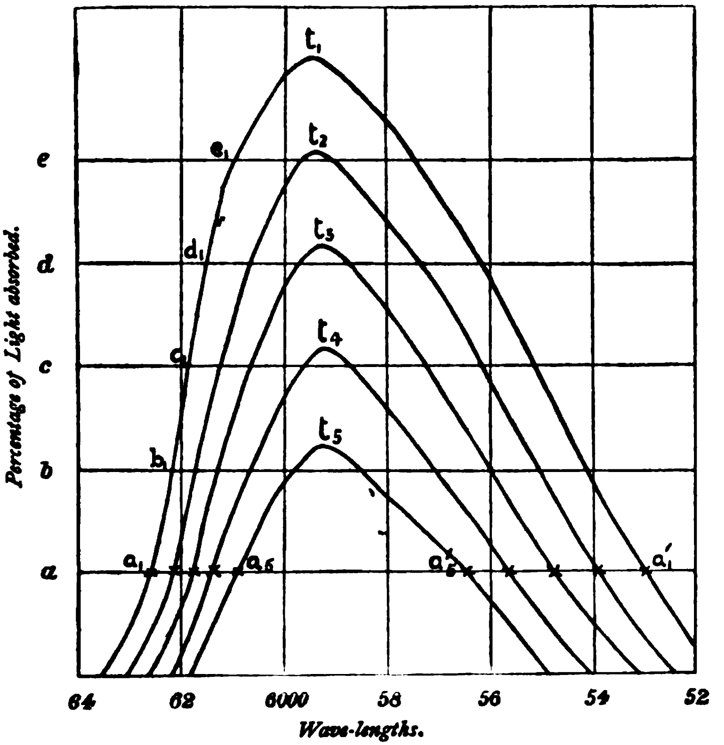


FIG. 13.

comes to the same thing, solutions of different concentrations in layers of the same thickness) by the spectrophotometer we can draw a family of curves as in Fig 13, the individual curves corresponding to thicknesses, t_1 t_2 t_3 t_4 t_5, etc.

From this family of curves we can construct a curve of the wave-length—thickness type. As we have already remarked, the edge of a band as measured by the ordinary spectroscope

D

is the point at which absorption has attained some appreciable value, it may be 5% or 10% or 20%, or some other value depending on the sensitiveness of the observer's eye or instrument. We can construct a wave-length — thickness curve for any desired percentage of absorption, say for A%. Draw a horizontal line cutting the vertical axis at a, and the family of curves at a_1 a_2 a_3 a_4 a_5, etc., a'_5 a'_4 a'_3 a'_2 a'_1, etc. These points

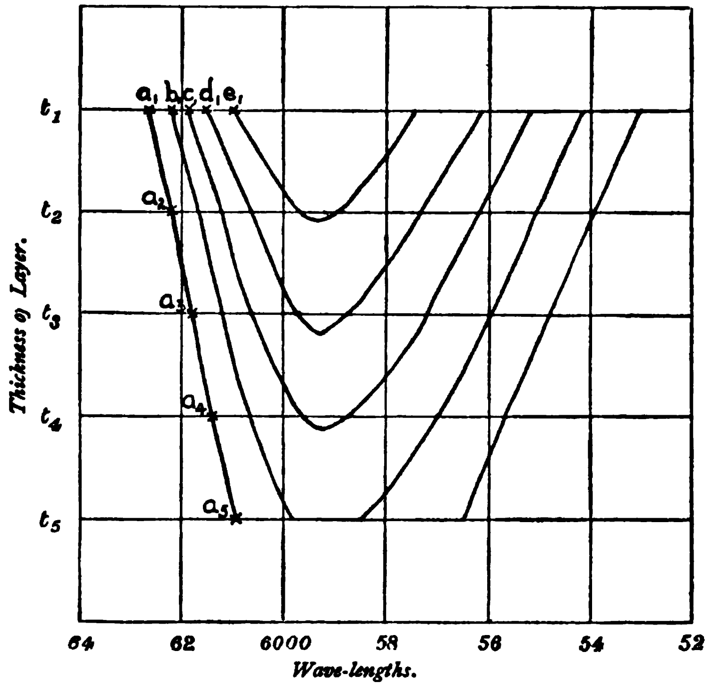


FIG. 14.

give the wave-lengths for which absorption has the value a for thicknesses, t_1 t_2 t_3 t_4 t_5, etc., and from them we can construct a curve, Fig 14 (a). In the same way we can construct a family of curves corresponding to percentages of absorption, a, b, c, d, e, etc. These are the curves we ought to get by observation in the ordinary spectroscope with eyes capable of detecting percentages of absorption, a, b, c, d, e, etc. And if the sensitiveness of an observer's eye remained constant

throughout a set of observations the curve drawn from them would correspond to one member of this family of curves. In Fig 13 the diagrammatic family of curves are steeper on the left than on the right hand side, and the new family constructed from them in Fig. 14 show the same peculiarity. Curves drawn from actual observation show that these characteristics are, as a matter of fact, handed on from the one family to the other (private communication from Prof. D. B.

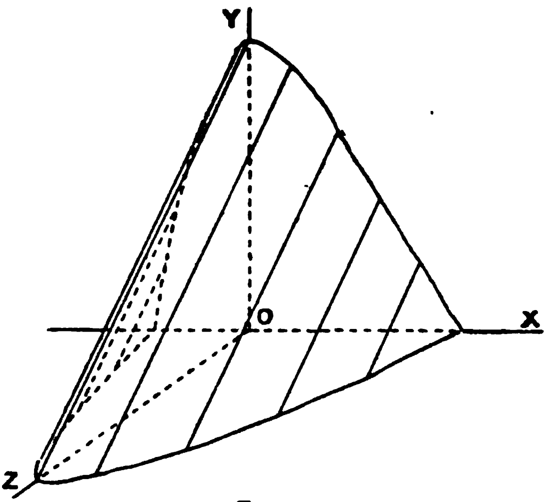


FIG. 15.
X = Wave-length.
Y = Intensity of light transmitted.
Z = Log thickness.

Meek). This justifies a remark previously made about the curves drawn from observation with the ordinary spectroscope, viz. that "they show at a glance whether the bands are symmetrical or not."

Theory also indicates this intimate connection between the two types of curve. We may regard the two families of curves as sections of a surface giving the percentage of light absorbed for all values of wave-length and thickness of layer. It will be most convenient to construct the surface with three rectangular axes (x,y,z) representing wave-length

(x), intensity of light transmitted (y) [light transmitted = original light *minus* light absorbed], and log thickness (z)—see Fig. 15.

Sections parallel to the plane xOy will give the family of curves "wave-length—light transmitted" and sections parallel to the plane xOz will give the family of curves "wave-length—log thickness."

Another family of curves is obtained by sections parallel to the plane yOz, viz., "light transmitted—log thickness" curves, giving the relationship between the thickness of the layer traversed and the proportion of light absorbed or transmitted. But according to Lambert's hypothesis—

$$\frac{I}{I_0} = e^{-kd}$$

where

I = intensity of light transmitted
I_0 = intensity of original light
d = thickness of layer traversed
k = a constant
e = base of natural logarithms

and this relationship is the same for light of all wave-lengths

$$\text{Our } y = \frac{I}{I_0}$$
$$\text{Our } z = \log d$$
$$\therefore\ y \propto z$$

and this family of curves is a set of parallel straight lines.

It is now obvious that we only need one "wave-length—light transmitted" curve and by the aid of Lambert's hypothesis we can construct the surface. It is in fact a cylinder of which the "wave-length—light transmitted" curves are oblique sections and the "wave-length—log thickness" curves another set of sections at right angles to them. This way of looking at the matter shows at once that the two families of curves will have the same characteristics, viz., if one set is symmetrical the other set will also be symmetrical; if one set is steeper on the side of shorter wave-lengths than on the side of longer wave-lengths, the other set will show the same peculiarity; or *vice versa*.

As regards the experimental justification for Lambert's hypothesis, Kayser (*Handbuch der Spectroscopie*, vol. III. pp. 16–19), gives a list of investigations which have been carried out on this subject. Bunsen and Roscoe (*Photometrische Untersuchungen*, 4 *Abh. Pogg. Ann. 101*, pp. 235–63, 1857) passed light through chlorine gas and compared the intensity of the light before and after its passage through the gas. Bernard (*Ann. chim. et phys.* (3) *35*, pp. 385–438, 1852) measured the absorption of light by layers of glass, potassium chromate, and copper sulphate of different thicknesses, using light which had been made to some extent homogeneous by passing through coloured glass. Beer (*Pogg. Ann. 86*, pp. 78–88, 1852) studied the absorption by solutions of copper sulphate and acetate and potassium ferrocyanide of light which had been filtered through red glass. Camichel (*Compt Rend. 117*, pp. 307–9, 1893) found the law correct for layers of liquid bromine whose thickness was varied between 0·5 and 60λ of sodium light. Bottomley (*Mem. Manchester Lit. and Phil. Soc.* (3), *7*, pp. 176–186, 1882; *Chem. News*, *42*, pp. 56–58) studied the absorption of light by layers of different thicknesses of a solution of nickel and cobalt salts which absorbed almost all kinds of light equally. Kayser summarises the results of these investigations by saying that they have found Lambert's hypothesis correct to the order of accuracy attained. Moreover the hypothesis can be taken as correct without hesitation, since many colorimetric methods are based on it and have been found to give correct results. At the same time he regrets that the hypothesis has not been more rigorously tested for homogeneous light.

Meek's investigations of the absorption spectra of triphenylmethane dyes by the spectrophotometer seem to indicate that the hypothesis is correct within fairly wide limits, but that eventually the intensity of the transmitted light falls off more rapidly than it should in accordance with the hypothesis. (Private communication from Prof. Meek.)

CHAPTER IV

ABSORPTION SPECTRA OF TYPICAL ORGANIC SUBSTANCES AND DYE-STUFFS

BEFORE proceeding to the discussion of further theories as to the relation between colour and constitution it will be convenient to mention the data which are now available as to the absorption spectra of dyes and coloured organic compounds and related substances; also to give a few typical examples. It may be mentioned that several theories have been put forward to the effect that the absorption spectra of dyes are those of the parent substances modified by the introduction of chromophores or auxochromes, or both, so that some of the absorption bands are brought forward into the visible part of the spectrum; and in this connection it is interesting to examine the absorption spectra of such substances as benzene, naphthalene, phenol, the di- and tri-hydroxybenzenes, aniline, nitrobenzene, azobenzene, anthraquinone, etc. Attempts have also been made to elucidate the cause of colour by studying some of the simplest substances in which colour is developed, such as the fatty compounds, diacetyl, tertiary nitroso-compounds, etc.; and it is interesting to compare the absorption spectra of such substances with those of the ordinary dyes and the more complicated aromatic coloured substances.

Attempts have also been made to get to the very root of the matter, and discover the very simplest structures giving selective absorption, *i.e.* absorption bands, in any part of the spectrum.

A list of substances, the absorption spectra of which had been studied up to that date in connection with the chemical constitution of organic compounds, will be found in the 1901

Report of the British Association for the Advancement of Science. Up to that time it may be said that practically the only investigators to record absorption spectra completely, *i.e.* by means of absorption curves, were Hartley and his collaborators, especially Dobbie, Huntington and Lauder. From that time onwards an increasing number of English chemists have taken up the study of absorption spectra by means of absorption curves, *e.g.* Baly and his collaborators Desch, Collie, Ewbank, Stewart, Edwards, Marsden, Tuck, Baker, Gazdar, Schaefer, Watson (H. E.), Lowry and Rice; also Hedley (partly in collaboration with Hartley), Hewitt and his collaborators Thomas, Buttle, Thole, Pope and Willett; Purvis and his collaborators Homer, Jones, Tasker and M'Cleland; and Watson (E. R.) and his collaborators Meek, Sen, Medhi, Sircar and Ghosh.

A good deal later a few German chemists adopted this method of investigation, especially Hantzsch and his collaborators, also Ley, Meyer, Fischer and Stobbe.

A new list of organic substances, of which the absorption spectra have been measured, has been prepared by Dobbie, Baly and Stewart in the 1916 *Report of the British Association for the Advancement of Science*, pp. 131–186.

But at the present time there is nothing like a systematic collection of absorption spectra, even of dyes and coloured organic substances. Formanek has studied the absorption spectra of dyes in a systematic but unfortunately only qualitative way (*Spektralanalytischer Nachweis künstlicher Organischer Farbstoffe*, Berlin, 1900), recording the positions of the maxima of absorption in very dilute solutions, and indicating whether the bands are symmetrical or not. And Mees has published photographs of the absorption spectra of a certain number of dyes, using a wedge-shaped cell to contain the solution through which the light was passed, and thus to a certain extent showing the change of absorption with variation of the thickness of the layer of solution examined (*An Atlas of Absorption Spectra*, by C. E. Kenneth Mees: Longmans).

The following reproductions of the absorption curves of

some typical organic substances are intended to give a general idea of the character of absorption bands :—

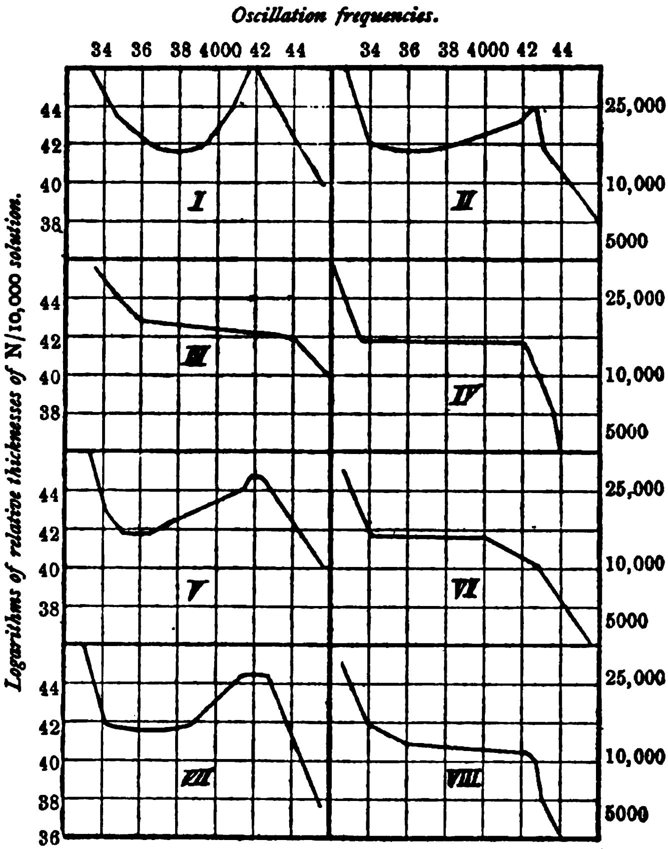


FIG. 16.

Acetone in alcohol	I	Methyl *iso*-propyl ketone . .	II
Acetone in water	III	Pinacoline	IV
Methyl ethyl ketone	V	Methyl hexyl ketone	VI
Methyl propyl ketone	VII	Methyl nonyl ketone	VIII

(Reproduced from Stewart and Baly's paper, *Chem. Soc. Trans.*, 1906, **89**, p. 492, Fig. 1.)

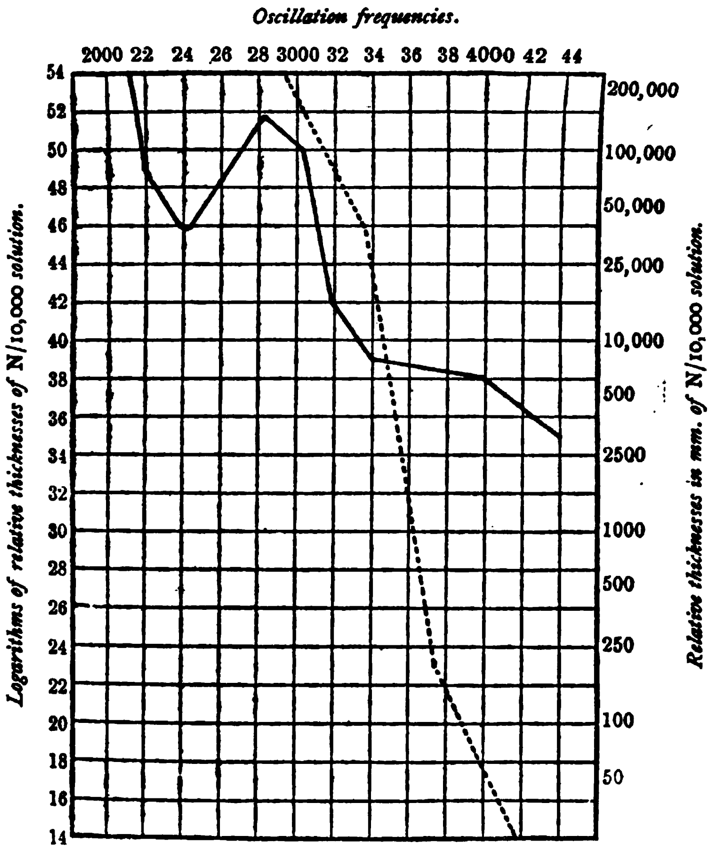


FIG. 17.

Diacetyl (full curve). Diacetyldioxime (dotted curve).

(Reproduced from Baly and Stewart's paper, *Chem. Soc. Trans.*, 1906, 89, p. 503, Fig. 1.)

Acetylacetone compounds.

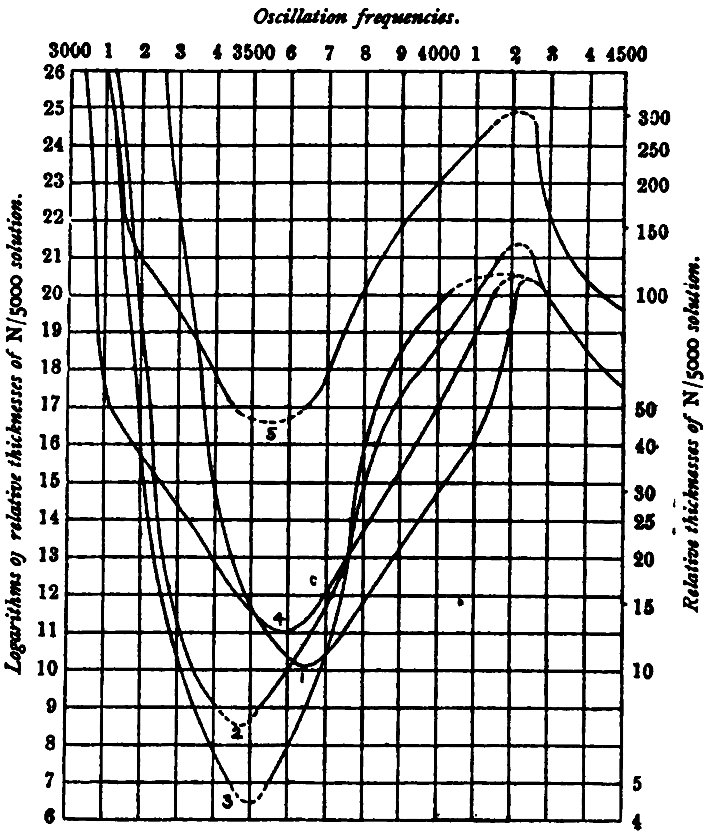


FIG. 18.

1. Acetylacetone.
2. Acetylacetone beryllium compound.
3. Acetylacetone aluminium compound.
4. Acetylacetone thorium compound.
5. Methylacetylacetone.

(Reproduced from Baly and Desch's paper, *Chem. Soc. Trans.*, 1904, 85, p. 1034, Fig. 2.)

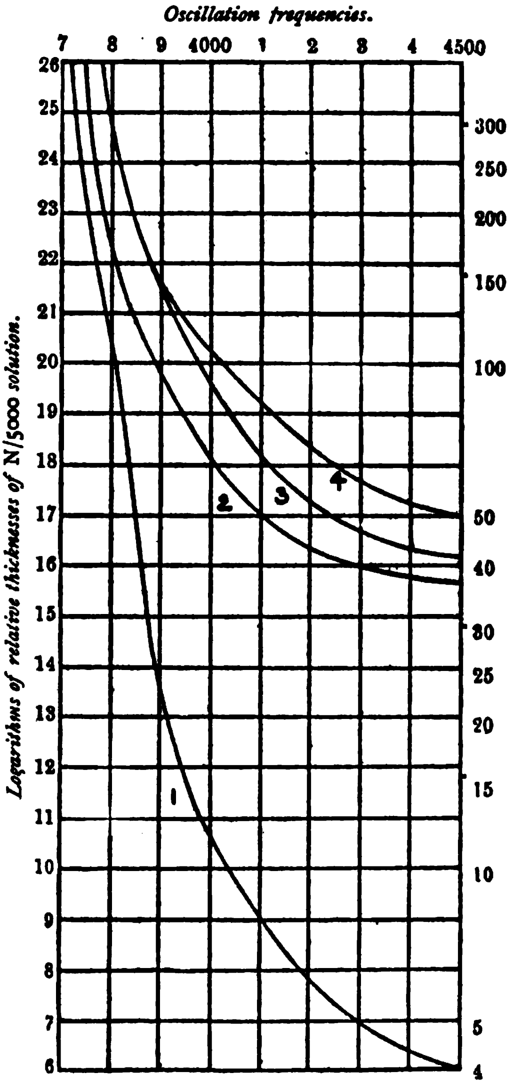


FIG. 19.

1. Ethyl ethoxycrotonate.
2. Ethyl acetoacetate.
3. Ethyl acetoacetate with a trace of hydrochloric acid.
4. Ethyl acetoacetate with excess of hydrochloric acid.

(Reproduced from Baly and Desch's paper, *Chem. Soc. Trans.*, 1904, 85, p. 1035, Fig. 3.

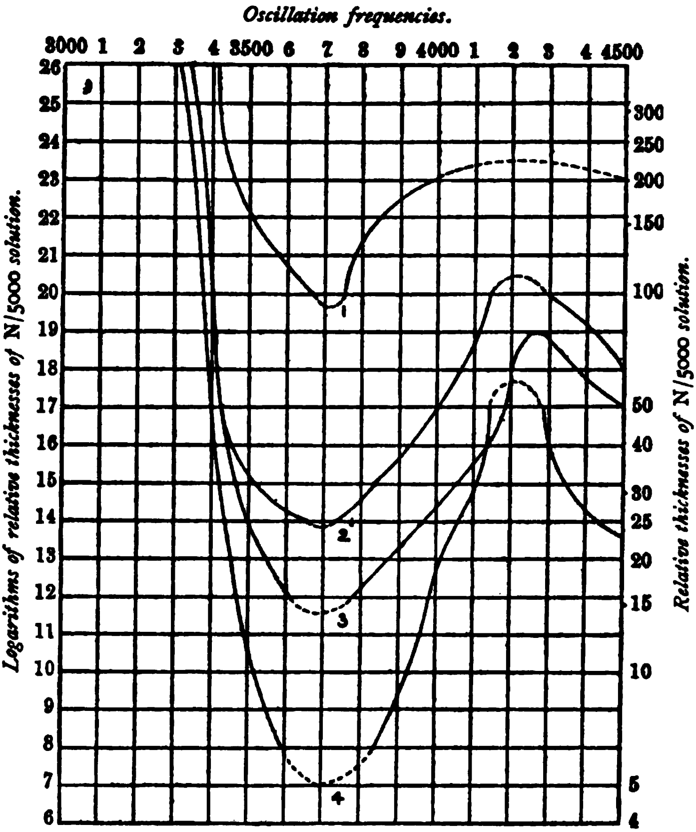


FIG. 20.

1. Ethyl acetoacetate in water with half an equivalent of NaOH.
2. Ethyl acetoacetate in water with one equivalent of NaOH.
4. Ethyl acetoacetate in water with excess of NaOH.
3. Ethyl acetoacetate, aluminium compound.

(Reproduced from Baly and Desch's paper, *Chem. Soc. Trans.*, 1904, 85, p. 1037.)

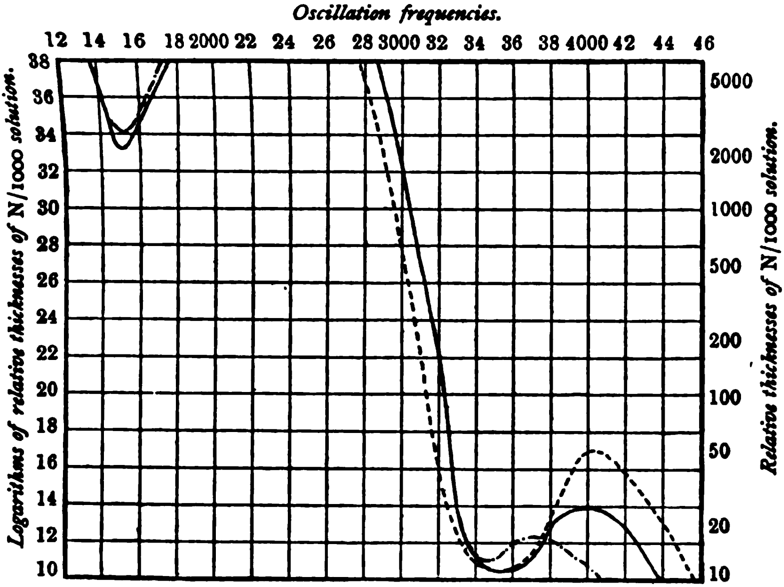


FIG. 21.

Full curve. *Tert.* nitroso*iso*propylacetone, blue solution in water.
Dotted curve. *Tert.* nitroso*iso*propylacetone, colourless solution in water.
Dot and dash curve. *Tert.* nitroso*iso*propylacetone, blue solution in alcohol.

(Reproduced from Baly and Desch's paper, *Chem. Soc. Trans.*, 1908, 93, p. 1754, Fig. 5.)

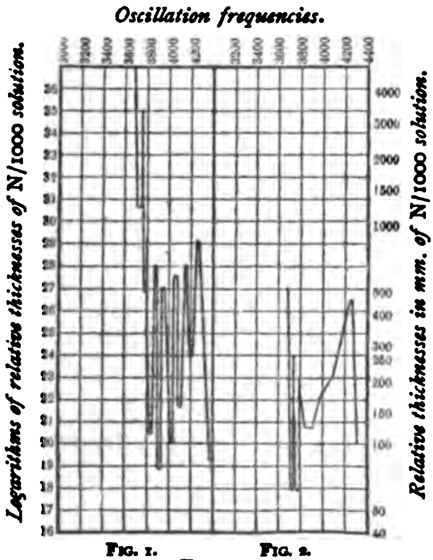


FIG. 22.

Benzene. Fig. 1. Ethyl benzene. Fig. 2.

(Reproduced from Baly and Collie's paper, *Chem. Soc. Trans.*, 1905, 87, p. 1342, Figs. 1 and 2.)

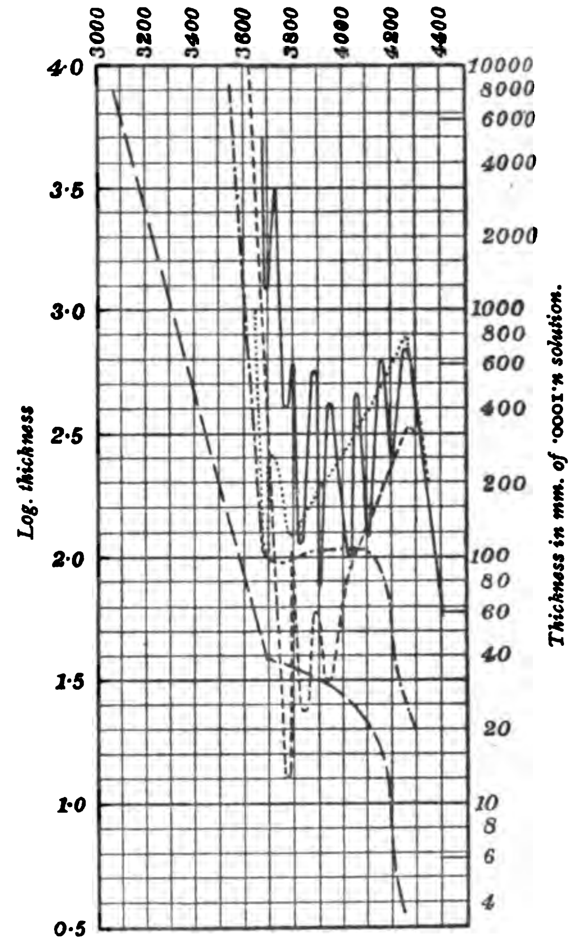


FIG. 23.

——— Benzene.
—·—· Brombenzene.
- - - - Fluorbenzene.
—— —— Iodbenzene.
...... Chlorbenzene.

(Reproduced from Ley's *Die Beziehungen zwischen Farbe und Konstitution*, 1911, Fig. 10, p. 78.)

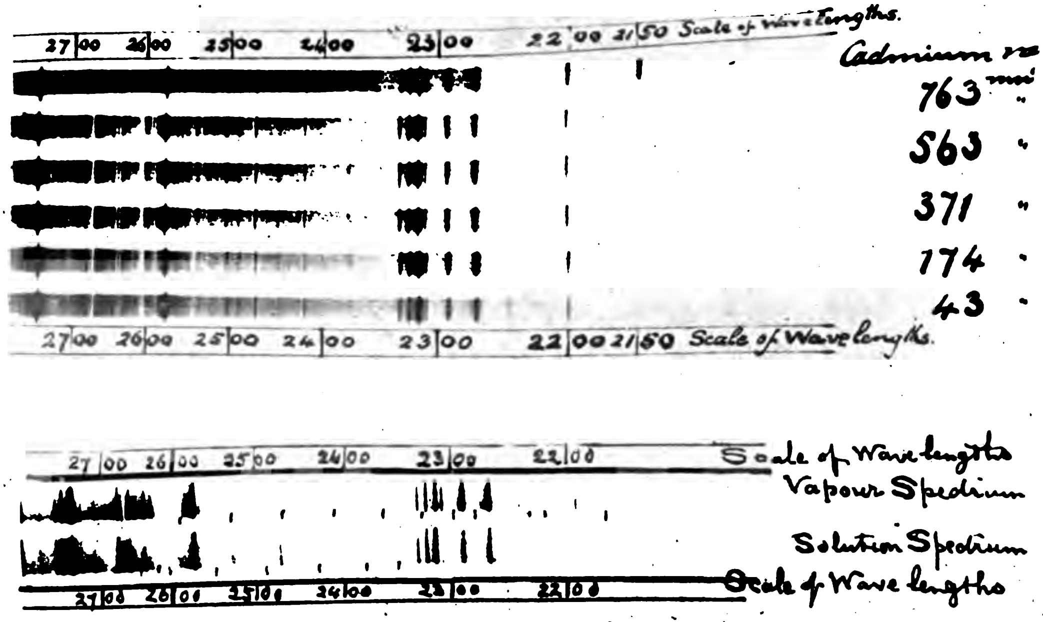


FIG. 24.—ABSORPTION SPECTRUM OF BENZENE VAPOUR UNDER REDUCED PRESSURE

(Reproduced from Hartley's paper, *Phil. Trans.* A 208 (1908), Plate 32, Figs. 6 and 7.)

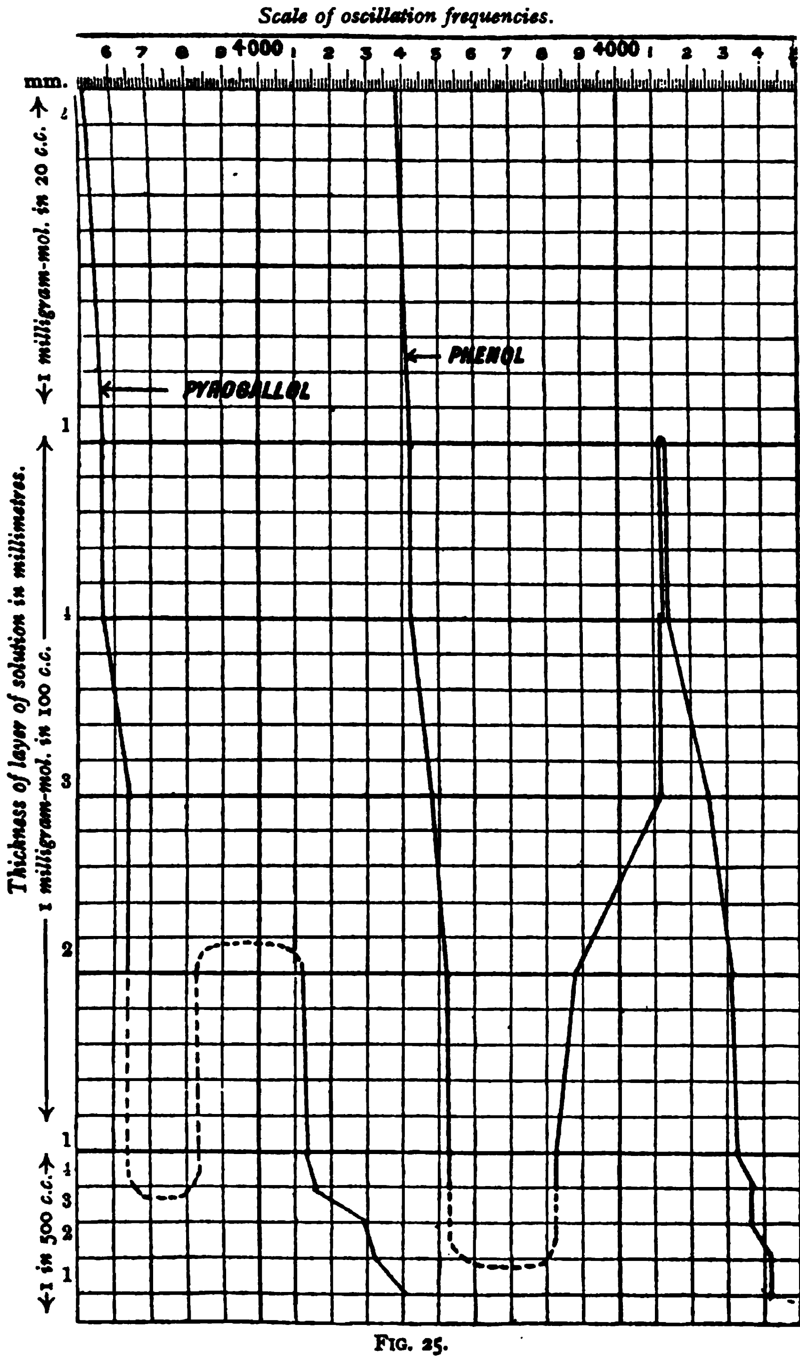


FIG. 25.
Phenol and pyrogallol.
(Reproduced from Hartley, Dobbie and Lauder's paper, *Chem. Soc. Trans.*, 1902, 81, p. 937.)

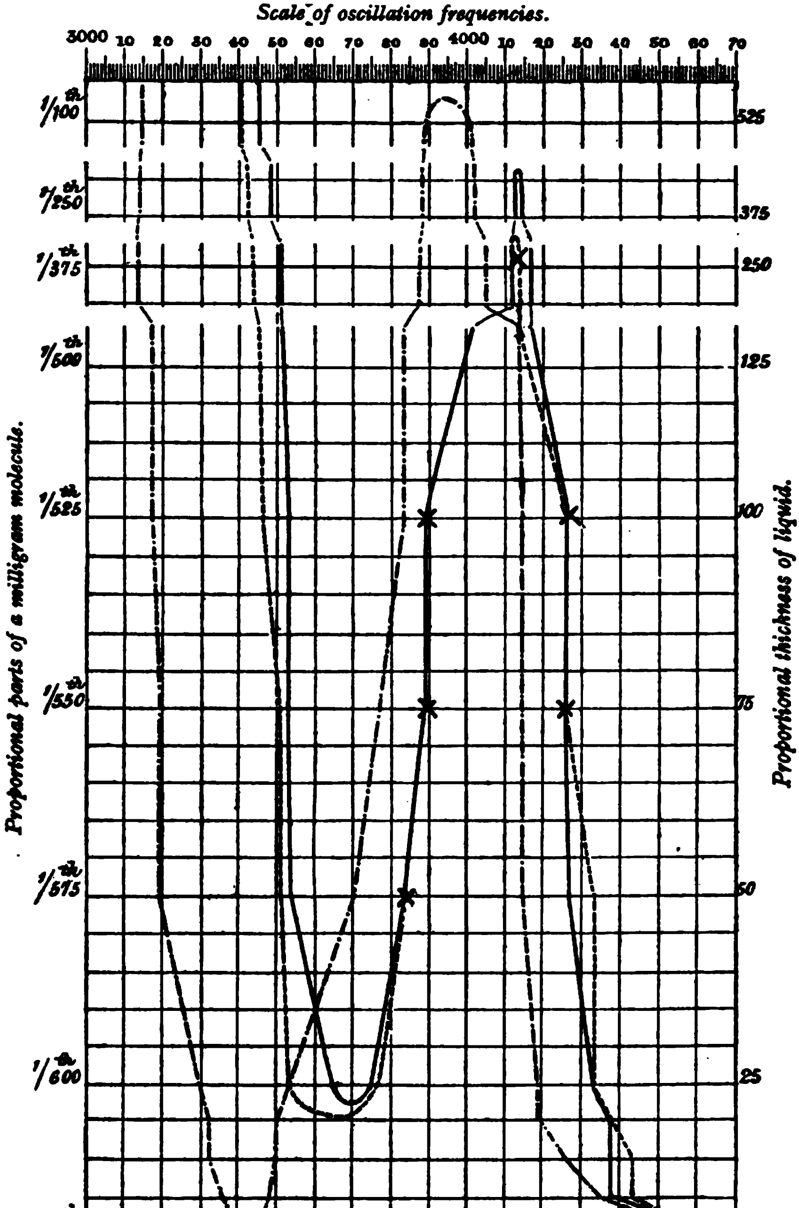


FIG. 26.—CURVES OF MOLECULAR VIBRATIONS.

—·—· Quinol.
- - - - - - Pyrocatechol.
——— Resorcinol.

The curves of Pyrocatechol and Resorcinol run one into the other at the points marked thus X.

(Reproduced from Hartley's paper, *Chem. Soc. Trans.*, 1888, 53, and Plate, facing p. 642.)

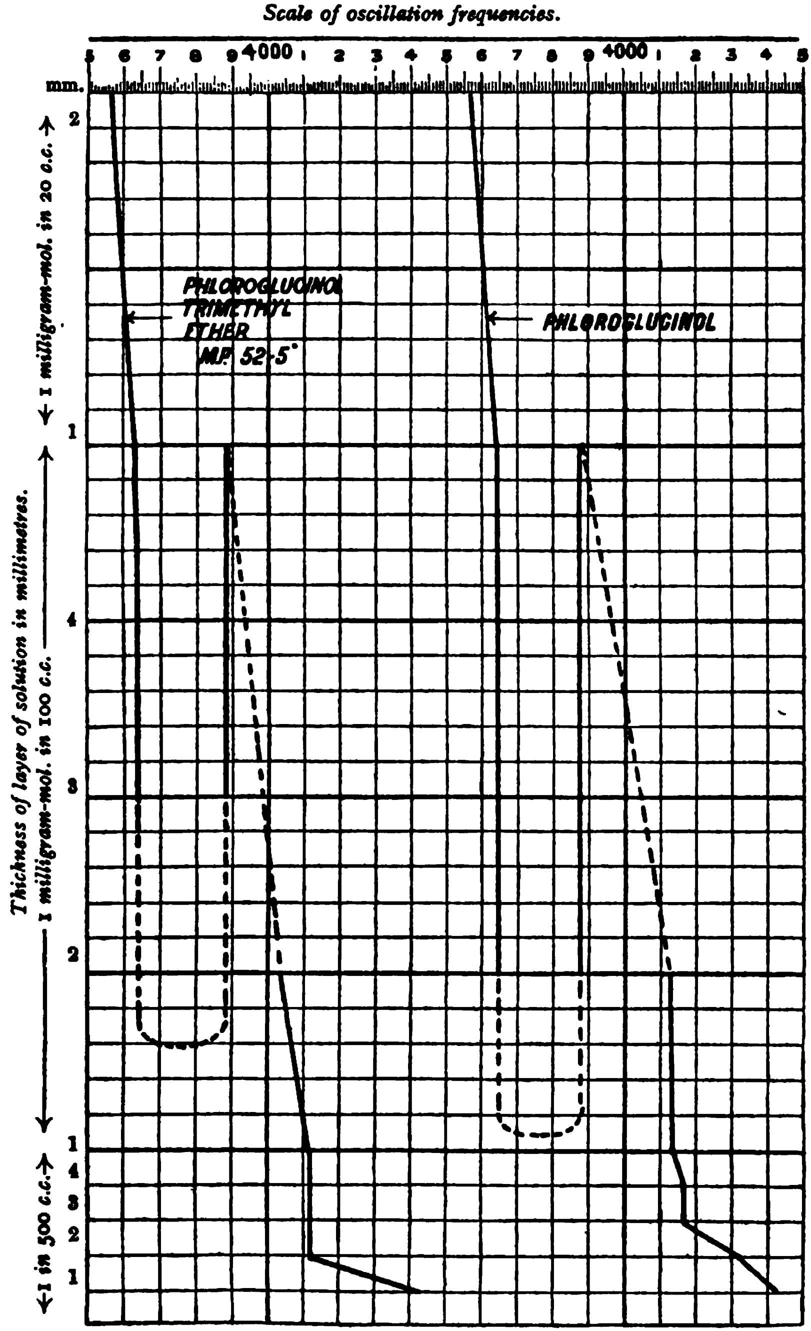


FIG. 27.

Phloroglucinol and phloroglucinol trimethyl ether.

(Reproduced from Hartley, Dobbie and Lauder's paper, *Chem. Soc. Trans.*, 1902, 81, p. 936.)

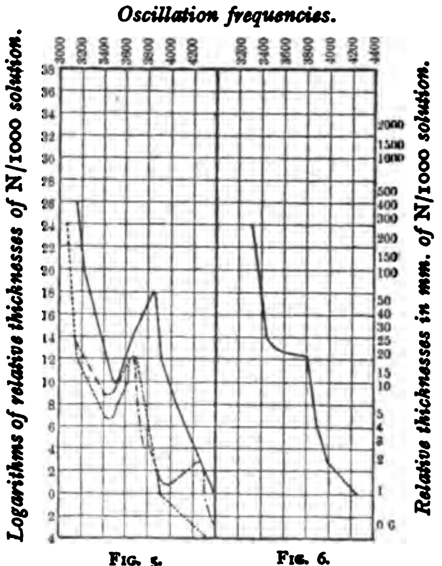


FIG. 28.

Aniline. Fig. 5, full curve. Methyl aniline. Fig. 5, dotted curve. Dimethyl aniline. Fig. 5, dot and dash curve. Acetophenone. Fig. 6.

(Reproduced from Baly and Collie's paper, *Chem. Soc. Trans.*, 1905, 87, p. 1343, Figs. 5 and 6.)

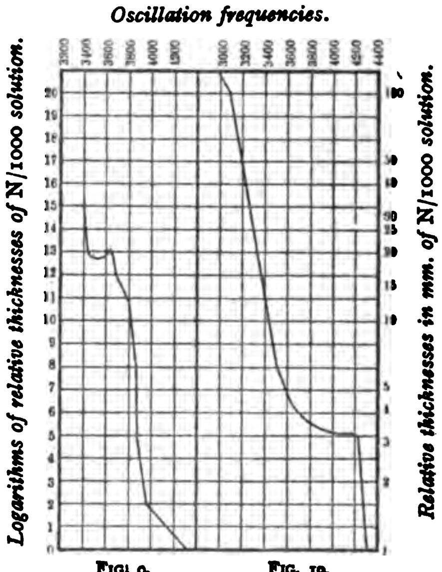


FIG. 29.

Benzaldehyde. Fig. 9. Nitrobenzene. Fig. 10.

(Reproduced from Baly and Collie's paper, *Chem. Soc. Trans.*, 1905, 87, p. 1344, Figs. 9 and 10.)

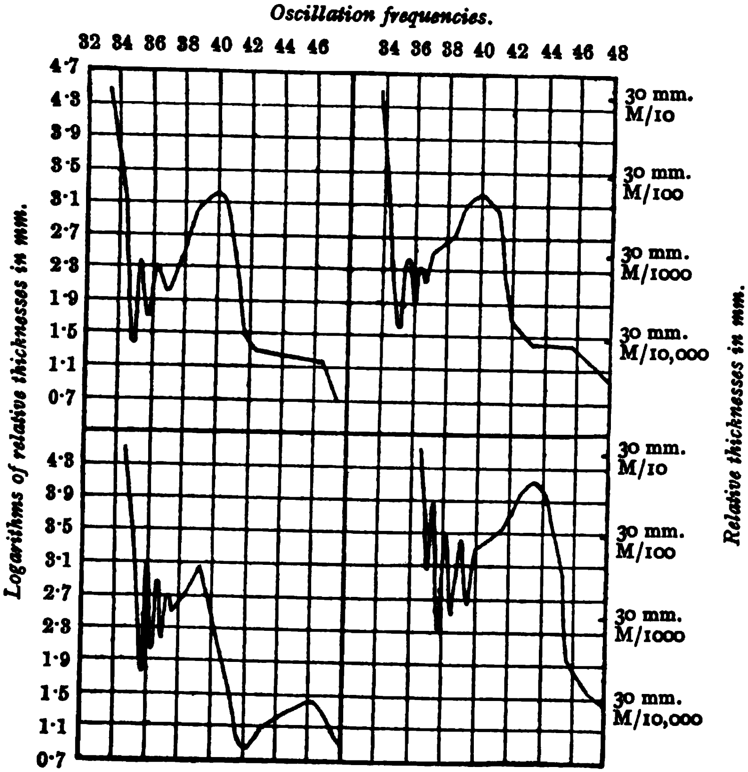


FIG. 30.

o-Toluonitrile, *m*-Toluonitrile. Upper curves.
p-Toluonitrile, Phenylacetonitrile. Lower curves.

(Reproduced from Purvis's paper, *Chem. Soc. Trans.*, 1915, p. 503, Fig. 2.)

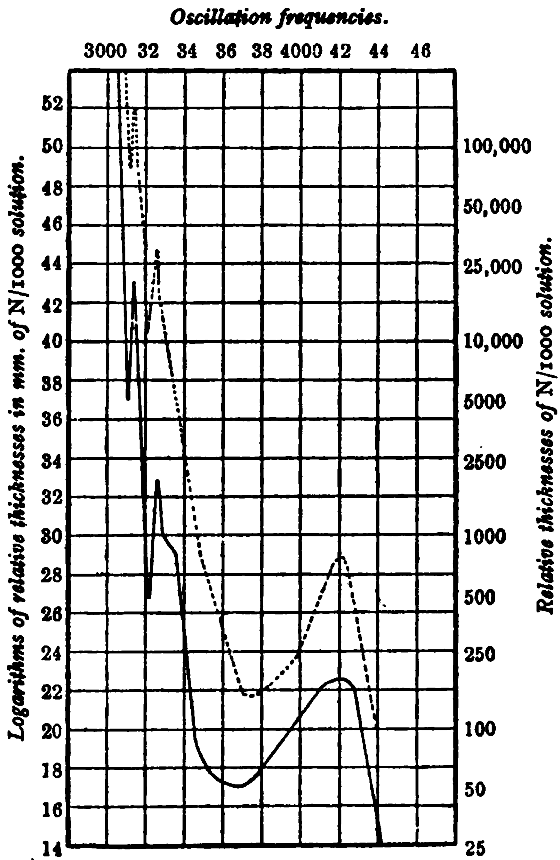


FIG. 31.

Naphthalene. Full curve.
Dihydronaphthalene. Dotted curve.

(Reproduced from Baly and Tuck's paper, *Chem. Soc. Trans.*, 1908, 93, p. 1903, Fig. 1.)

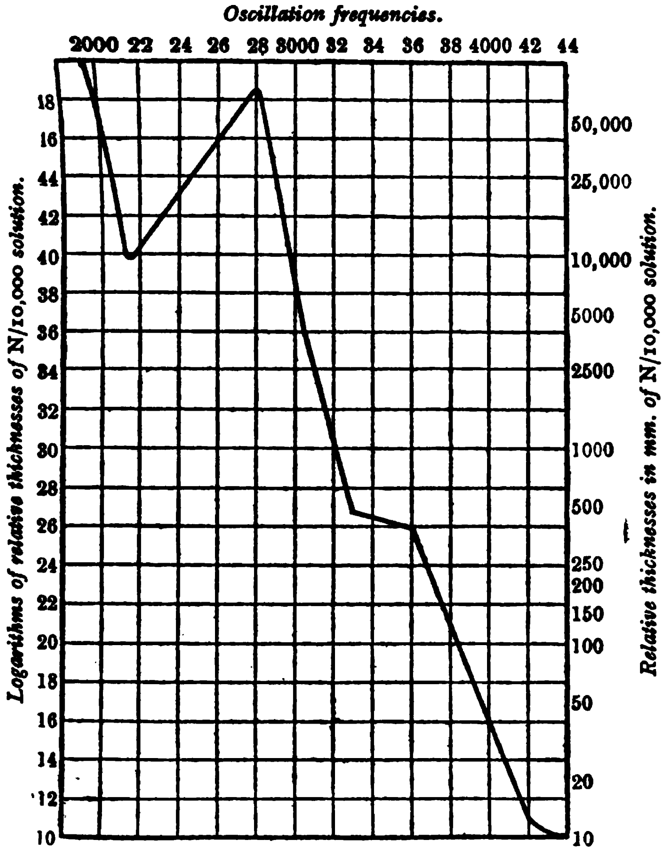


FIG. 32.

Benzoquinone.

(Reproduced from Baly and Stewart's paper, *Chem. Soc. Trans.*, 1906, 89, p. 507, Fig. 4.)

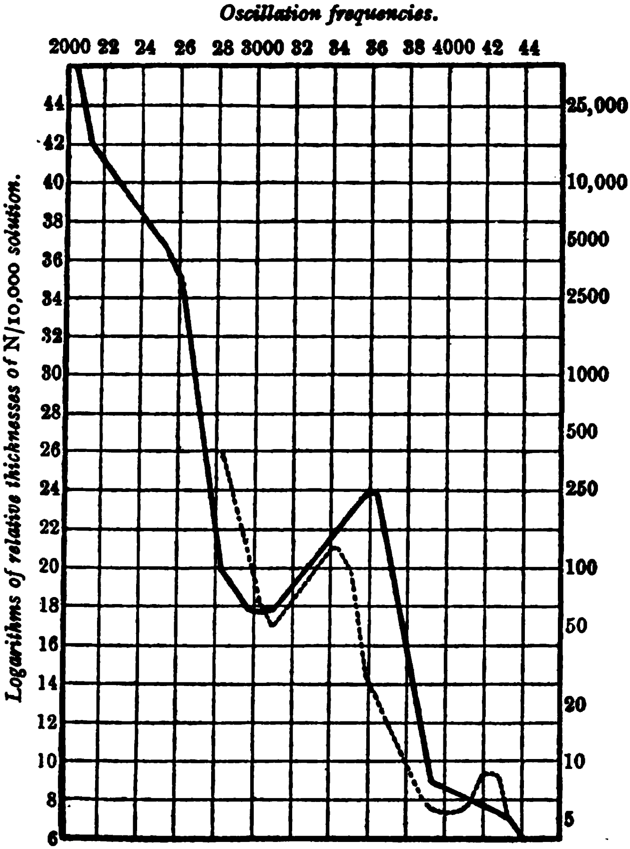


FIG. 33.

α-Naphthaquinone. Full curve.
Anthraquinone. Dotted curve.

(Reproduced from Baly and Stewart's paper, *Chem. Soc. Trans.*, 1906, **89**, p. 511, Fig. 8.)

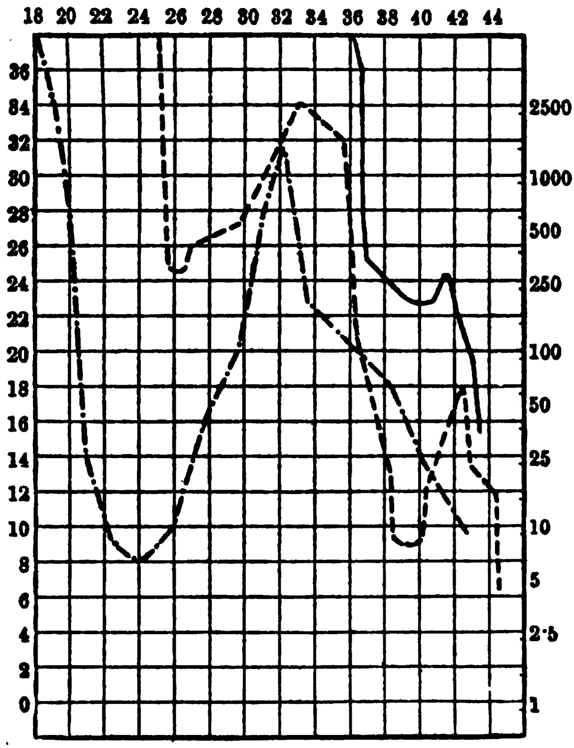


FIG. 34.

Full curve. Triphenyl methane.
Dotted curve. Triphenyl methane (Hartley).
Dot and dash. Triphenyl carbinol sulphate.

(Reproduced from Baker's paper, *Chem. Soc. Trans.*, 1907, 91, p. 1494, Fig. 4.)

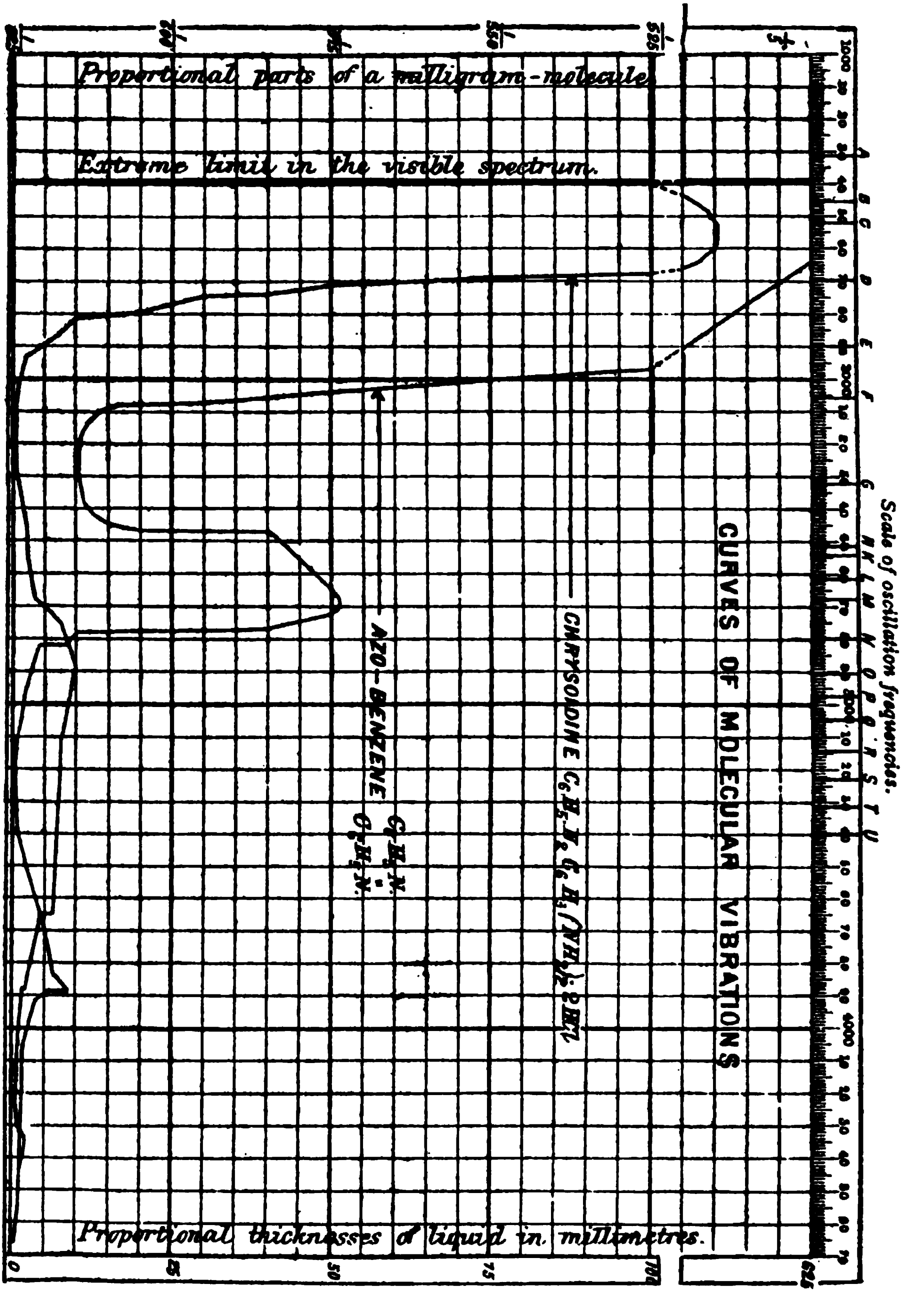


FIG. 35.
Azobenzene and chrysoidine.
(Reproduced from Hartley's paper, *Chem. Soc. Trans.*, 1887, 51, p. 152, *et seq.*, Plate IV.)

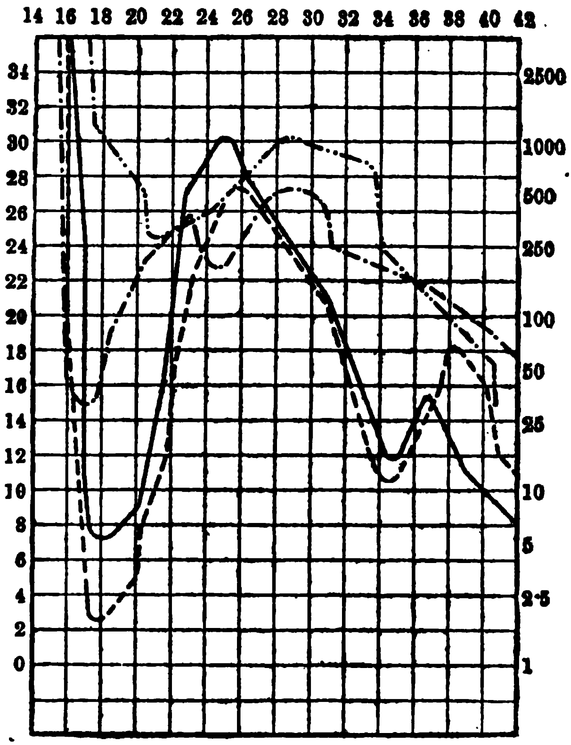


FIG. 36.

Full curve. **Pararosaniline.**
Dotted curve. **Pararosaniline hydrochloride.**
Dash and dot curve. **Pararosaniline in N. hydrochloric acid.**
Dash and two dots. **Pararosaniline in conc. hydrochloric acid.**

(Reproduced from Baker's paper, *Chem. Soc. Trans.*, 1907, 91, p. 1498, Fig. 7.)

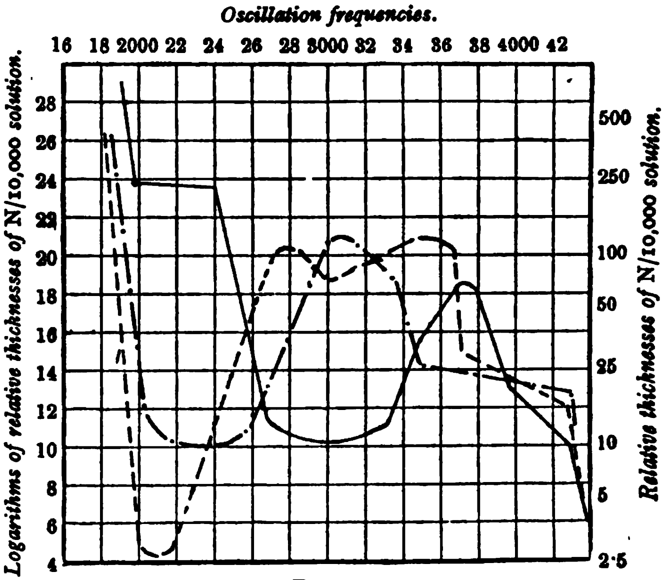


FIG. 37.

Full curve. Benzeneazophenol in alcohol.
Dotted curve. Benzeneazophenol in conc. HCl.
Dot and dash curve. Benzeneazophenol in alcoholic NaOEt.

(Reproduced from Tuck's paper, *Chem. Soc. Trans.*, 1907, 91, p. 450, Fig. 1.)

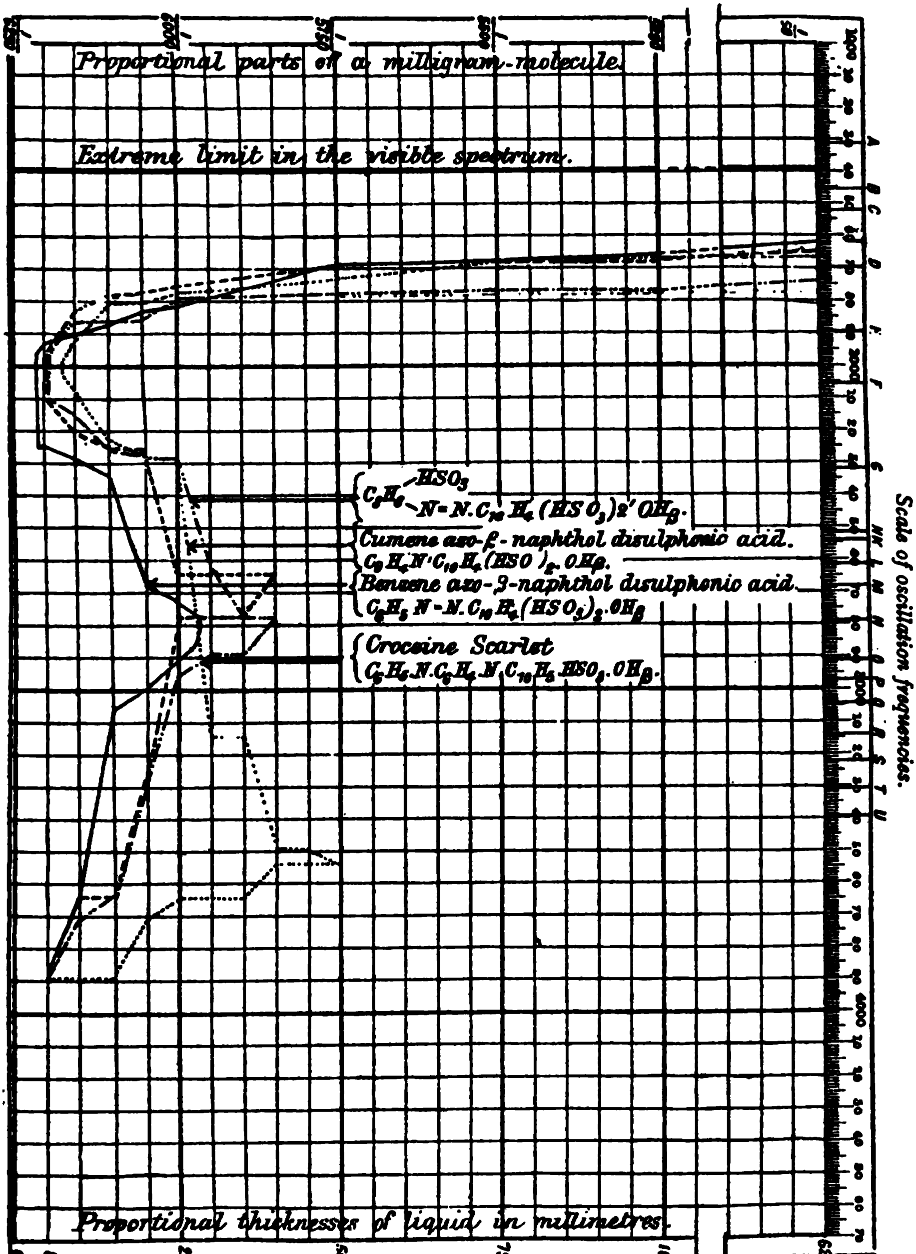


FIG. 38.

$$C_9H_9\begin{cases} SO_3H \\ N = N - C_{10}H_4(SO_3)_2OH\beta \end{cases}$$

Cumene-azo-β-naphthol disulphonic acid.
Benzene-azo-β-naphthol disulphonic acid.
Crocein Scarlet.

(Reproduced from Hartley's paper, *Chem. Soc. Trans.*, 1887, 51, pp. 152 *et seq.* Plate VIII.)

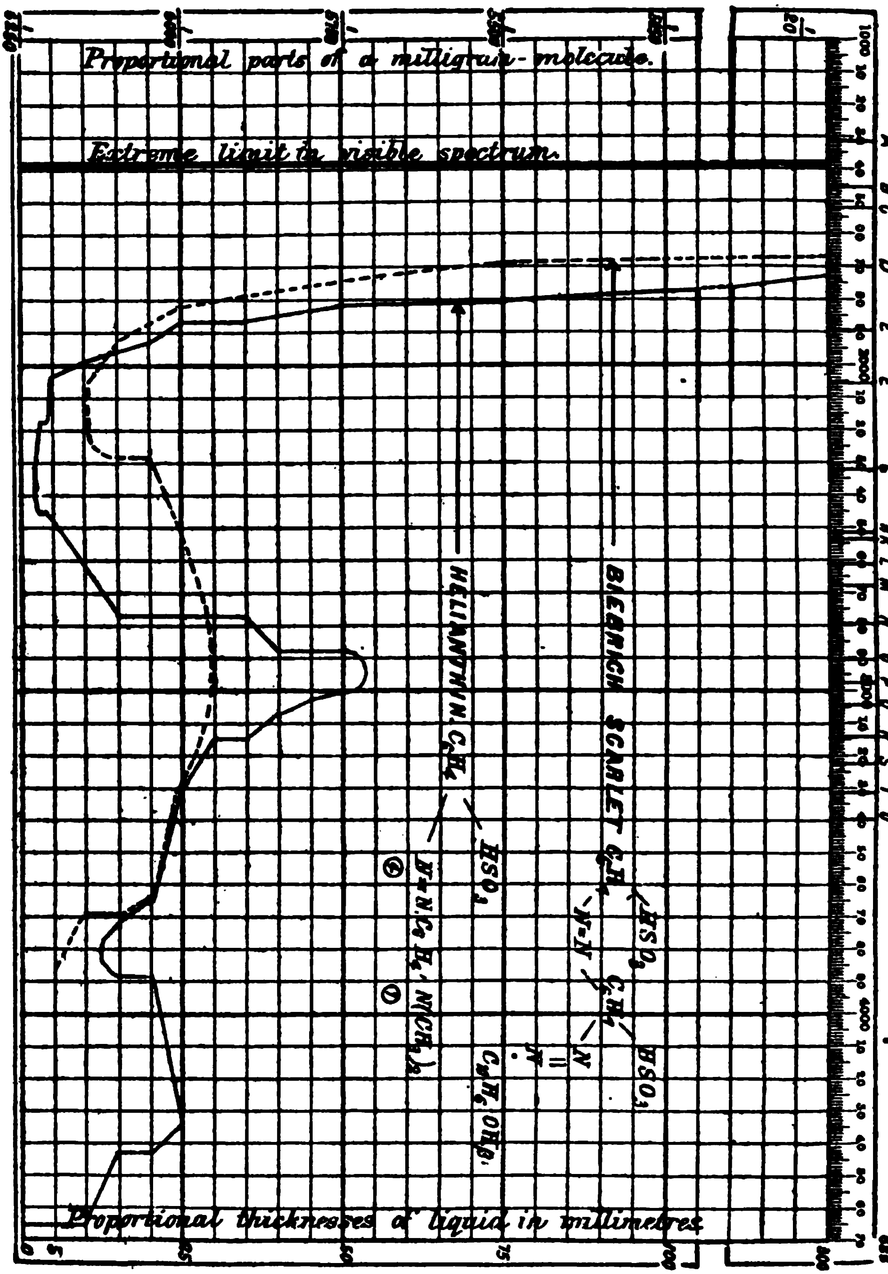


FIG. 39.

Helianthin. Biebrich Scarlet.

(Reproduced from Hartley's paper, *Chem. Soc. Trans.*, 1887, 51, pp. 152 *et seq.* Plate VII.)

1/1000 *solution.*

FIG. 40.

$$\text{Fast Red} = C_{10}H_6\begin{cases}[4]SO_3Na \\ [1]N = N - [1]C_{10}H_6[2]OH\end{cases}$$

[NOTE.—In this and the following photographs from Mees' *Atlas* the absorption bands are black. The figures indicate approximate wave-lengths. The top of the photograph corresponds to a layer fifteen times as thick as the bottom.]

(Reproduced from *An Atlas of Absorption Spectra*, by C. E. Kenneth Mees, D.Sc., of the Eastern Kodak Research Laboratory, Rochester, New York, Fig. 26.)

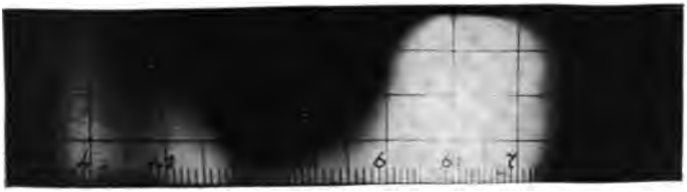
1/1000 *solution.*

1/2000 *solution.*

FIG. 41.

$$\text{Congo Red} = \begin{array}{l} C_6H_4[4] - N = N - [2]C_{10}H_5\begin{cases}[1]NH_2 \\ [4]SO_3Na\end{cases} \\ [1]\,| \\ C_6H_4[4] - N = N - [2]C_{10}H_5\begin{cases}[1]NH_2 \\ [4]SO_3Na\end{cases}\end{array}$$

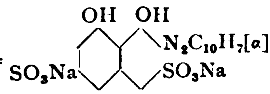
(Mees' *Atlas*, Figs. 42 and 43.)



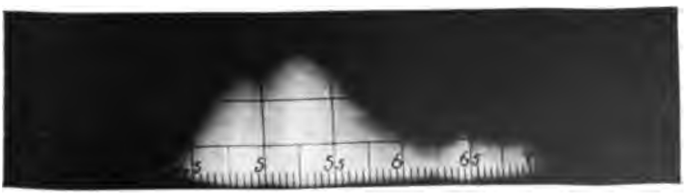
1/2500 *solution.*

FIG. 42.

Chromotrope 10B =



(Mees' *Atlas*, Fig. 85.)



1/1000 *solution.*

FIG 43.

Eboli Green.

Benzidine < Salicylic acid
α-naphthylamine—1·8 dioxynaphthalene sulphonic acid
(or something similar)

(Mees' *Atlas*, Fig. 158.)

In the absence of absorption curves for the more complicated azo-dyes the following data from Formanek are given for a few typical cases (Fig. 44).

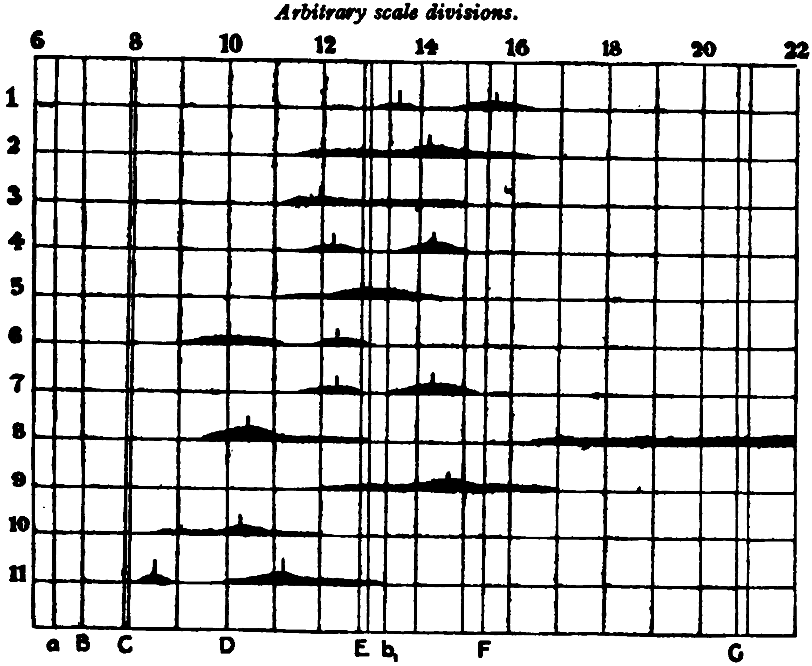
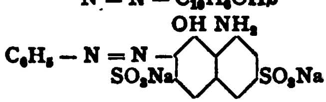


FIG. 44.

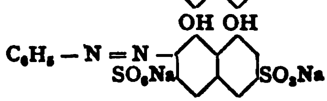
1. Orange II $C_6H_4 \langle {SO_3Na(4) \atop (1)N = N - (1)\ C_{10}H_6(2)OH}$

2. Fast Red A $C_{10}H_6 \langle {SO_3Na \atop N = N - C_{10}H_6OH\beta}$

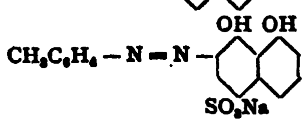
3. Fast Acid Fuchsine B



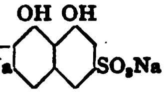
4. Biebrich Acid Red 4B



5. Azofuchsin B



[*Continued on next page.*

6. **Azo Acid Blue B** $NH_2C_6H_4-N=N-$ 

7. **Ponceau 4 RB = Croceine Scarlet 3B** $C_6H_4\left\{\begin{array}{l}(4)\ SO_3Na\\(1)\ N=N-C_6H_4-N=N-(1)\ C_{10}H_5\begin{array}{l}(2)\ OH\\(8)\ SO_3Na\end{array}\end{array}\right.$

8. **Diamond Green** $C_6H_3\left\{\begin{array}{l}OH\\COOH\\-N=N-C_{10}H_6-N=N-(2)\ C_{10}H_4SO_3Na(4)\end{array}\right.$ with $OH(1)$, $OH(8)$ on the $C_{10}H_4$

9. **Congo Red** Benzidine $\left\langle\begin{array}{l}\text{naphthionic acid}\\\text{naphthionic acid}\end{array}\right.$

10. **Diamine Blue 3B** Tolidine $\left\langle\begin{array}{l}\text{H acid}\\\text{H acid}\end{array}\right.$

11. **Azo Blue** Tolidine $\left\langle\begin{array}{l}\text{NW acid}\\\text{NW acid}\end{array}\right.$

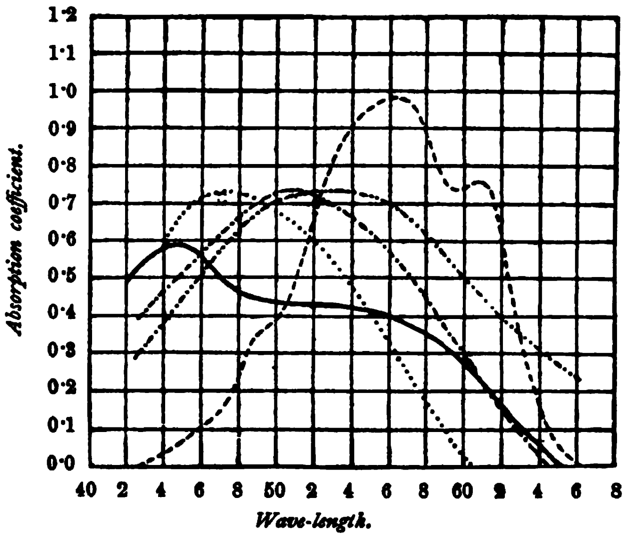


FIG. 45.

Alizarin or 1:2-dihydroxyanthraquinone.

——— Alizarin in alcohol, $N/10^4$, 10 mm. thickness.
- - - - „ in KOH, $N/10^4$, 10 mm. thickness, 400 mols KOH.
. . . . . . „ on tin mordanted wool, ½ per cent. dyeing.
—·—·— „ on alum mordanted wool, ½ per cent. dyeing.
—··—·— „ on chrome mordanted wool, ½ per cent. dyeing.

(Reproduced from Meek and Watson's paper, *Chem. Soc. Trans.*, 1916, 109, p. 545.)

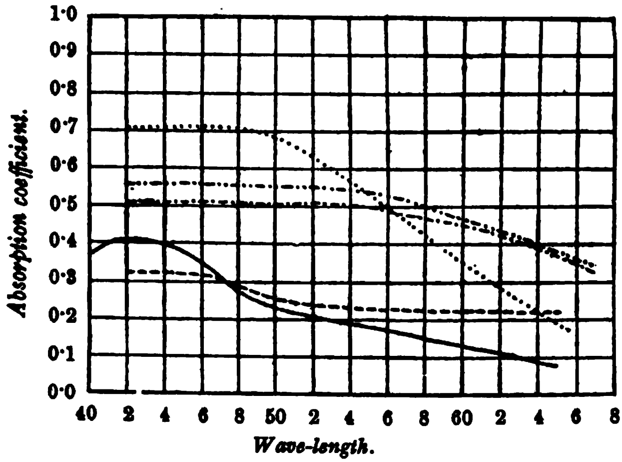


FIG. 46

Anthragallol or 1:2:3-trihydroxyanthraquinone.

——— Anthragallol in alcohol, N/10⁴, 10 mm. thickness.

- - - ,, in KOH, N/10⁴, 10 mm. thickness, 400 mols KOH

. . . . . . ,, on tin mordanted wool, ½ per cent. dyeing.

—·—·— ,, on alum mordanted wool, ½ per cent. dyeing.

—··—··— ,, on chrome mordanted wool, ½ per cent. dyeing.

(Reproduced from Meek and Watson's paper, *Chem. Soc. Trans.*, 1916, 109, p. 548.)

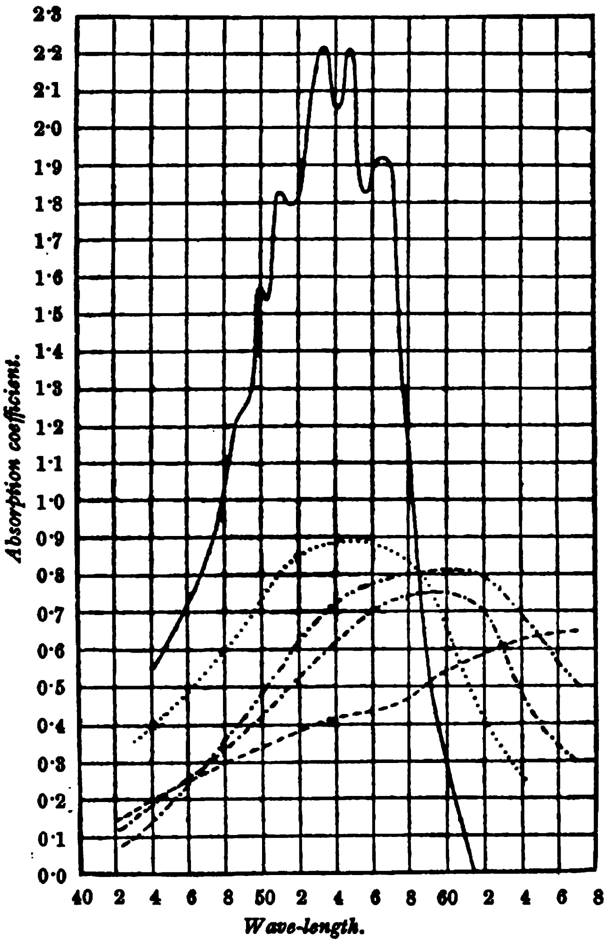


FIG. 47.

Anthracene-blue or 1:2:4:5:6:8-hexahydroxyanthraquinone.

————	Anthracene-blue	in alcohol, N/10[4], 10 mm. thickness.
– – – –	,,	in KOH, N/10[4], 10 mm. thickness, 400 mols KOH.
. . . . . .	,,	on tin mordanted wool, ½ per cent. dyeing.
—–—–	,,	on alum mordanted wool, ½ per cent. dyeing.
—·—·—	,,	on chrome mordanted wool, ½ per cent. dyeing.

(Reproduced from Meek and Watson's paper, *Chem. Soc. Trans.*, 1916, 109, p. 551.)

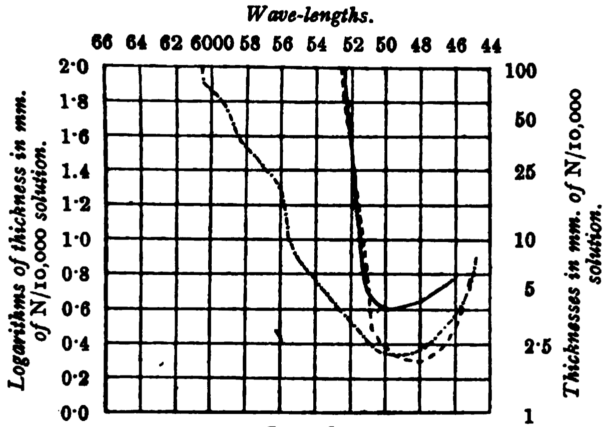


FIG. 48.

——— Fluorescein in alcoholic solution.
- - - - Dihydroxyfluorescein in alcoholic solution.
—·—·— Gallein in alcoholic solution.

(Reproduced from Medhi and Watson's paper, *Chem. Soc. Trans.*, 1915, p. 1579, Fig 1.

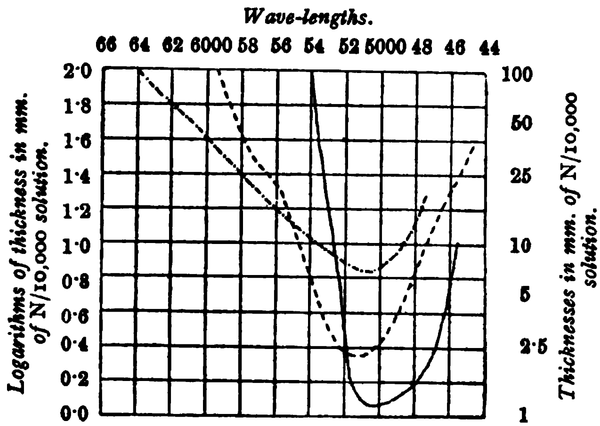


FIG. 49.

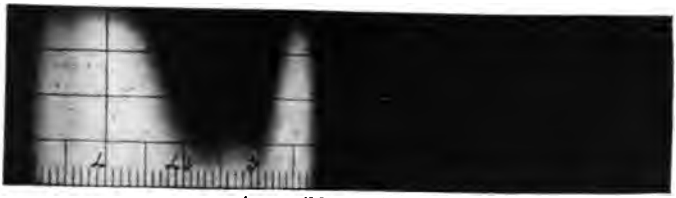
——— Fluorescein in alcohol solution with 20 mols KOH.
- - - - Dihydroxyfluorescein in alcoholic solution with 20 mols KOH.
—·—·— Gallein in alcoholic solution with 30 mols KOH.

(Reproduced from Medhi and Watson's paper, *Chem. Soc. Trans.*, 1915, p. 1580, Fig. 3.

F

It will be seen that in all the cases given the number of absorption bands in the visible and ultra-violet parts of the spectrum is strictly limited and the bands are very broad. It may be mentioned here that saturated fatty compounds show no absorption bands, but only general absorption in the extreme ultra-violet, and it is generally considered that unsaturation is the cause of selective absorption in the visible and ultra-violet parts of the spectrum.

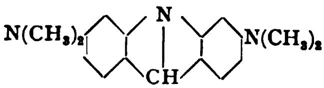
But this view may require reconsideration. Apparently saturated hydrocarbons show no selective absorption either in the visible or ultra-violet parts of the spectrum. [On the other hand they do show selective absorption in the infra-red, and it appears as indefensible to draw a hard-and-fast line between the infra-red and the visible parts of the spectrum as it is to separate arbitrarily the visible and ultra-violet parts.] Neither do unsaturated fatty hydrocarbons show selective absorption in the visible or ultra-violet. This does not seem in agreement with the view that unsaturation is the cause of selective absorption. When we come to the consideration of organic compounds other than hydrocarbons we have to face the possibility that selective absorption may be due to elements other than carbon and hydrogen. Baly's recent discussion of the fine ultra-violet absorption bands of sulphur dioxide under reduced pressure will help to remind us that very simple compounds of some elements which frequently occur in organic compounds may possess selective absorption. Nitrogen peroxide is a well-known example of the same kind. Even some of the elements themselves possess selective absorption: *e.g.* sulphur, either in the solid, liquid, or gaseous condition; and apparently oxygen also possesses faint selective absorption. The blue colour of ozone and water is well-known, as are also the rain-bands in the spectrum of sunlight which has passed through the earth's atmosphere. Russell and Lapraik (*Chem. Soc. Trans.* 1881, *39*, 168 *et seq.*) have reported that many simple compounds, such as water, ammonia, alcohol, etc., show quite sharp absorption bands in the visible and ultra-violet parts of the spectrum if examined in sufficiently thick layers.



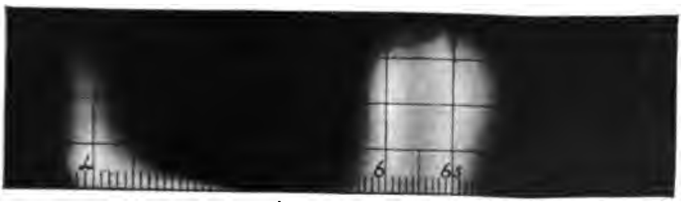
1/5000 (*blue end only*).

FIG. 50.

Acridine Orange.



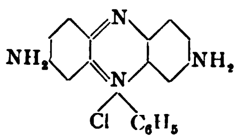
Mees' *Atlas*, Fig. 19.)



1/2000 *solution*.

FIG. 51.

Phenosafranine.

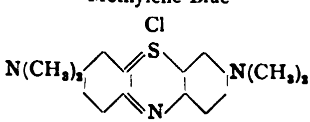


(Mees' *Atlas*, Fig. 70.)

1/10,000 *solution*.

FIG. 52.

Methylene Blue



(Mees' *Atlas*, Fig. 120.)

These observations of Russell and Lapraik may be mentioned in a little more detail. It was found that almost all liquids when examined in columns from 2 to 8 ft. in length exhibited absorption bands in the visible part of the spectrum. Carbon bisulphide and carbon tetrachloride were exceptions. The positions of the bands for some of the liquids examined were approximately as follow:—

Substance	*Positions of bands* (λ)
Water . .	Infra-red to 6550, 6100–6000
Methyl alcohol .	Infra-red to 6700, 6320–6290
Ethyl alcohol .	Infra-red to 6700, 6340–6290
Propyl alcohol .	Infra-red to 6900, 6330–6290
Amyl alcohol .	Infra-red to 6900, 6330–6290
Ethyl iodide .	Strong absorption from 7240 to 7160, weaker absorption on to 6980, 6310–6250
Amylene . .	Infra-red to 6700, 6340–6290
Amyl iodide .	Absorption identical with that of amylene
Chloroform .	7170–7110, 6160–6070
Ether . .	Infra-red to 6900, 6160–6070
Acetaldehyde .	Infra-red to 6400, 6300–6250
Acetic acid .	Infra-red to 6270, 6150–6100
Benzene . .	Strong absorption from 7140 to 7030, weaker absorption on to 6780, still weaker on to 6300, 6160–6060
Toluene . .	Infra-red to 7250, 7140–7030, 6500–6300, 6160–6060
Xylene . .	Infra-red to 7250, 7150–7050, 6400–6300 6160–6060
Monochlorbenzene .	7140–7030, 6160–6060
Dichlorbenzene	7140–7030, 6060 (very faint)
Naphthalene .	7140–7030, 6300, 6160–6060
Phenol . .	7100–6790, 6100–6000
Ammonia (in water)	Infra-red to 6820, 6520–6490, 6300, 6120–6080, 5600
Methylamine .	Infra-red to 6860, 6570–6520, 6300
Ethylamine .	7220–7100, 6620–6550, 6300, 6120–6080

The general character of the bands is shown in Fig. 53 reproduced from the original paper.

If we remember that the absorption bands of ordinary organic dye-stuffs are generally visible in something like 10 mm. of $^{M}/10{,}000$ solution we can calculate that they are, roughly speaking, about 33,000,000 times as strong as those observed by Russell and Lapraik.

Nevertheless, such cases cannot be dismissed by saying that the absorption is very slight. In some cases, as for example nitrogen peroxide, this is not so. So that it would appear at any rate possible to argue that the selective absorption of organic compounds is due to the elements other than carbon and hydrogen contained in them. For example, the absorption bands of all hydroxy compounds might be regarded as water bands intensified and shifted by the replacement of hydrogen by an organic radicle. Similarly amino-compounds might be regarded as derivatives of ammonia; nitro, nitroso compounds, etc., as derivatives of the oxides of nitrogen; and so on.

Benzene shows more numerous and narrower bands than most other substances. A few simple benzene derivatives, such as fluor-benzene, benzonitrile, the toluonitriles, phenyl-acetic acid and tribenzylamine, have several fairly narrow bands similar to those of benzene; but most substances, including the simplest derivatives of benzene, have only one or two bands, and these are much broader than those of benzene. Most dye-stuffs show only one or two broad bands. The poly-hydroxy-anthraquinones show more bands than most dye-stuffs. Alizarine cyanine and Anthracene blue W.R. show five or six bands in alcoholic solution and a larger number in some other solvents, *e.g.* Alizarine cyanine shows ten in amyl ether. It seems possible that the broad absorption bands shown by most organic substances may consist of a considerable number of much narrower bands which have fused together, or, rather, which cannot be resolved under ordinary conditions. Pauer first showed that whereas benzene vapour at atmospheric pressure has a very similar spectrum to that of liquid benzene, or of solutions of

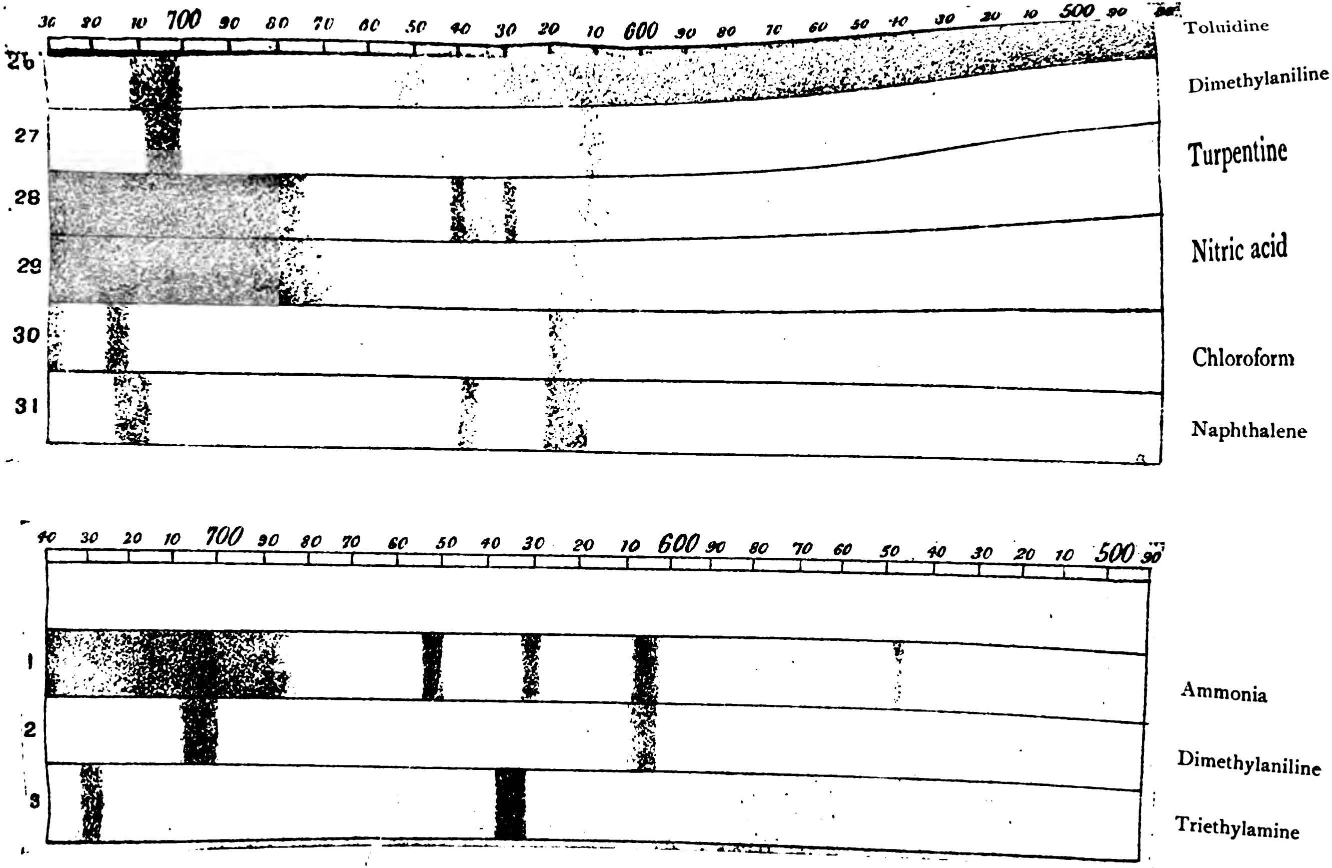


FIG. 53.—ABSORPTION SPECTRA OF APPARENTLY COLOURLESS LIQUIDS EXAMINED IN THICK LAYERS
(Reproduced from Russell and Lapraik's paper, *Chem. Soc. Trans.*, 1881, 39, 168 *et seq.*)

benzene in alcohol, etc., the vapour at lower pressures gives an absorption spectrum consisting of a large number of very narrow bands (see Fig. 24). Under similar conditions chlorbenzene, toluene, aniline, phenol, benzaldehyde, benzonitrile and the toluonitriles also show a large number of fine bands. So also does benzoquinone. But such fine bands have not yet been observed in the absorption spectra of the majority of substances under any circumstances.

It may be that the ordinary broad bands consist of these finer bands fused together. In fact, Hartley came to this conclusion with regard to benzene after a careful comparison of the ordinary and the fine banded absorption spectra.

It seems, however, that some other investigators would not be inclined to regard the broad bands as formed by the fusion of the narrower bands, even when they occur in the same part of the spectrum. (See M'Cleland, *Phil. Mag.* 1915 [vi.], *29*, 192). Apparently they hold the view that the narrower bands may be rendered more visible in the part of the spectrum where the broad bands give some general absorption, in somewhat the same way as stars are said to be visible at mid-day to an observer looking up a tall chimney or from the bottom of a well. This view will probably be rather difficult definitely to disprove. But the more obvious view will find general acceptance if an extended number of substances can be induced to exhibit fine banded absorption, and if in all cases the groups of fine bands occupy the same positions as the ordinary broad absorption bands.

Mrs. Laird's study of the absorption spectrum of chlorine gas (*Astrophys. Journ.*, *14*, 85 [1901]), seems to indicate that in this case the fine absorption lines and the broad absorption band observed were due to different causes. The fine lines extended from $\lambda=4800$ to $\lambda=5350$ at atmospheric pressure, and to $\lambda=5450$ at $2\frac{1}{2}$ atmospheres. The line spectrum scarcely altered in character at all with increasing pressure, the lines only becoming blacker and new lines being added towards the red. There is also a general absorption band

in the ultra-violet which could not be resolved into lines even when the pressure was reduced to 5 cm. It was found to vary very much in extent with change of pressure, and at the greater pressures it extended even over the absorption lines, reaching $\lambda=4990$ at $2\frac{1}{2}$ atmospheres.

This investigation seems to suggest a way of deciding whether the fine bands of benzene vapour, etc., are produced by the resolution of the broad bands. Observation of benzene vapour at different pressures with a spectrophotometer should decide whether the broad bands disappear when the fine bands come into view.

If the broad absorption bands are not formed by the fusion of a large number of much narrower bands, then it is certain that they must be caused by some kind of forced vibration within the molecule, the vibration being opposed by a great deal of friction. The absorption curves show that most of the bands are asymmetrical, and theory indicates that this would be the case for bands due to forced vibrations.

CHAPTER V

RELATIONSHIPS BETWEEN CONSTITUTION AND DEPTH OF COLOUR

NIETZKI'S RULE: *The colour of a dye-stuff can be deepened by adding groups so as to increase its molecular weight, and the deepening of colour produced is more or less proportional to the increase of its molecular weight.*—This rule has been referred to in Chapter I. It was probably formulated by Nietzki to summarize well-known facts in connection with the triphenylmethane group of dyes, but apparently was not based on any systematic investigation. The table given in Chapter I. shows that the rule applies to a considerable extent to other groups besides the triphenylmethane series. The rule was subjected to a careful examination by Schütze (*Z. f. physikalische Chem.* 1892, *9*, 109 *et seq.*) who pointed out many exceptions. His investigation showed that the effect of an added atom or group depended not only on its weight, but also on its chemical nature, and on the position in which it attached itself to the molecule. He pointed out that in some cases, *e.g.* on the addition of a nitro-group to indigo, the shade even becomes lighter instead of deeper and the terms *bathychrome* and *hypsochrome* were introduced: the former being applied to those groups which produce a deepening of colour, and the latter to those having the contrary effect. Another example of a hypsochrome is the acetyl group. All dye-stuffs containing hydroxyl or amino-groups become much lighter in colour when completely acetylated, in some cases becoming quite white. Within a few years of the announcement of Nietzki's rule several investigators recorded the positions of the maxima of the absorption bands of a

number of dyes and their derivatives (Vogel, *Ber.* 1887, *20*, 712–718; Krüss, *Z. f. physikalische Chem.* 1888, *2*, 312–337; *ibid.* 1895, *18*, 559–562; *Ber.* 1883, *16*, 2051–2056; *ibid.* 1885, *18*, 1426–1433; Bernthsen, *Ann.* 1885, *230*, 73–211; *ibid.* 1887, *20*, 924–934; Bernthsen and Gorke, *Ber.* 1887, *20*, 924–934). As the colour of a substance is determined by the position of its absorption band (or bands), and is deeper the nearer the band (or bands) lie to the red end of the spectrum, these investigations served as a quantitative study of Nietzki's rule. It was found to be generally true that the introduction of alkyl groups or halogen atoms shifted the absorption bands towards the red, and thus deepened the colour.

Substance.	Solvent.	Position of the absorption maximum (or maxima) in wave-lengths $\mu\mu$.	Observer.
Indigo	chloroform	604·8	Krüss and Oeconomides
Methyl indigo	"	619·7	
Ethyl indigo	"	652·6	"
Bromindigo	"	606·3	"
Dibromindigo	"	623·0	"
Benzene-azo-β-naphthol sulphonic acid B	alcohol	503·0	" Vogel
Toluene-*o*-azo-β-naphthol sulphonic acid B	"	510·0	"
Toluene-*p*-azo-β-naphthol sulphonic acid B	"	512·0	"
Thionin	"	610·0	Bernthsen and Gorke
Dimethyl thionin	"	625·0	"
Diethyl thionin	"	655·0	"
Fluoresceïn	aqueous alkali	494·0	Krüss
Dibromfluoresceïn	"	504·8	"
Tetrabromfluoresceïn	"	515·9	"

On the other hand it was shown that in some cases the introduction of nitro groups shifted the absorption band (or bands) towards the blue end of the spectrum, and consequently made the colour lighter instead of deeper, *i.e.* the nitro group acted as *hypsochrome*.

Substance.	Solvent.	Positions of the absorption maxima in wave-lengths $\mu\mu$.		Observer.
Indigo	chloroform	604·8		Krüss and Oeconomides
Nitro-indigo	,,	585·8		,,
Fluoresceïn	aqueous alkail	494·0		Krüss
Tetranitro-fluoresceïn	,,	489·0		,,
Alizarin	concentrated H_2SO_4	609·5	499·4	,,
β-nitroalizarin	,, ,,	518·3	490·4	,,

[It may be pointed out, however, that the nitro-group has not always this hypsochromic effect. Colourless substances, such as phenol and aniline, become coloured when nitro-groups are introduced into the molecule and, as will be mentioned later under Hewitt's rule, the introduction of a nitro-group into benzene-azo-phenol, converting it into *p*-nitrobenzene-azo-phenol, has a very strong bathychromic effect, judging by the colours of the alkaline solutions.]

According to some observations of Krüss the amino-group had also a hypsochrome effect:—

Substance.	Solvent.	Position of the absorption maximum in wave-lengths $\mu\mu$.
Alizarin	chloroform	609·5
Amido-alizarin	,,	531·5
β-amido-alizarin	,,	540·3
Alizarin	concentrated H_2SO_4	499·4
Amido-alizarin	,, ,,	495·2
Indigo	,, ,,	605·1
Amido-indigo	,, ,,	588·9

[Here also it should be remarked that the amino-group does not always exert a hypsochromic effect. On the contrary, being an auxochrome, it generally has a very marked bathychromic effect: *e.g.* yellow anthraquinone is converted into red α-aminoanthraquinone, colourless fuchsonimine is converted into Döbner's violet by an amino-group, and aminoazobenzene is deepened in colour by a second amino-group converting it into chrysoidine.]

The following small table is of interest as showing that in some cases the molecular weight may be made very large without a deep colour being attained.

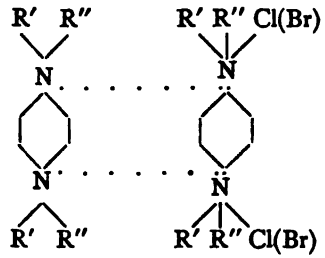
Molecular Formula.	Mol. wt.	Shade of Dyeing.
$C_6H_5-N=N-C_6H_4OH$	198	yellow
$C_6H_5-N=N-C_6H_4-N=N-C_6H_3{}^{OH}_{COOH}$	346	brownish yellow
$C_6H_5-N=N-C_6H_4-N=N-C_6H_4-N=$ $N-C_6H_3{}^{OH}_{COOH}$	450	brownish yellow
$C_6H_5-N=N-C_6H_3{}^{OH}_{C_6H_5}$	274	orange
$C_6H_4-N=N-C_6H_3{}^{OH}_{COOH}$ $\vert$ $C_6H_4-N=N-C_6H_3{}^{OH}_{COOH}$	482	yellow
$(OH)C\begin{cases} C_6H_4-N=N-C_6H_3{}^{OH}_{COOH} \\ C_6H_4-N=N-C_6H_3{}^{OH}_{COOH} \\ C_6H_4-N=N-C_6H_3{}^{OH}_{COOH} \end{cases}$	752	yellow

Colours of the Second Order

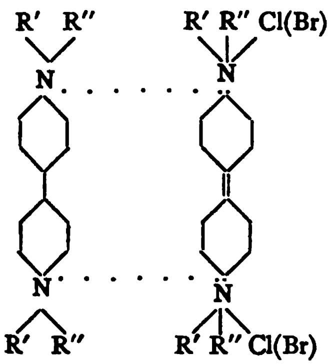
Before concluding the discussion of Nietzki's rule reference may be made to Piccard's conception of "colours of the second order" and the experimental facts which led him to announce that he had realized such a colour of the second order (*Ber.* 1913, *46*, 1843, *et seq.*).

By the limited oxidation of *p*-phenylenediamine there is obtained a strongly coloured substance of the same character as quinhydrone. One molecule of *p*-phenylenediamine is oxidized to quinone-diimide and combines with another molecule of unchanged *p*-phenylenediamine. Similar compounds are formed by the oxidation of derivatives of *p*-phenylenediamine in which the amino-groups are alkylated or arylated. These compounds form salts.

Without troubling as to the exact mode of union of the quinonoid and non-quinonoid halves of the molecule their formulæ may be written—



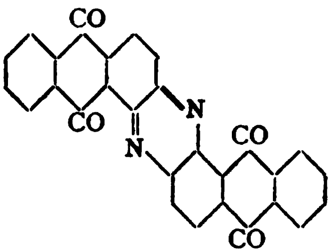
They are termed *meri*-quinonoid salts, and the series forms a good illustration of Nietzki's rule as the colour becomes progressively deeper the more completely the molecule is alkylated or arylated and the heavier the substituent groups are made. *Meri*-quinone di-imonium bromide is yellow. The corresponding salt from diphenyl-*p*-phenylenediamine is blue and that from tetraphenyl-*p*-phenylenediamine is green. By the oxidation of benzidine and alkylated or arylated benzidine a similar series of *meri*-quinonoid salts are formed which may be represented as—



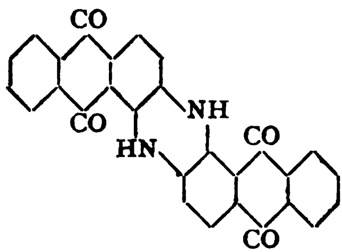
The *meri*-quinonoid salt from benzidine has a deeper colour than that from *p*-phenylenediamine, and so on throughout the series. That from tetraphenylbenzidine should have the deepest colour of all. As a matter of fact it is yellow. The deepening of colour in any series such as this is due to the gradual movement of the absorption band from the blue to the red end of the spectrum, and it is only to be expected that the band might eventually pass

altogether out of the visible spectrum into the infra-red. This appears to have happened in the case of the *meri*-quinonoid salt from tetraphenylbenzidine, and the yellow colour is apparently due to a second band which has come forward from the ultra-violet into the visible part of the spectrum. Hence it is called yellow "of the second order." It is very desirable that the first band should be detected in the infra-red, but this has not yet been done. Straus and Zeime (*Ber.* 1913, *46*, 2267) regard the colour of auramine as yellow of the second order, but, as will be explained later, there is no necessity for this.

SCHOLL'S RULE.—The very first publication which was ever made on the relation between constitution and colour (Graebe and Liebermann, *Ber.* 1868, *1*, 106; see Chapter I) pointed out that the colour of organic compounds seemed to depend on some degree of unsaturation, and that reduction destroyed their colour. The term *leuco-compound*, applied to substances obtained by the reduction of dye-stuffs, *e.g.* indigo-white from indigo, or to substances which on gentle oxidation yield dye-stuffs, *e.g.* the leuco-compounds of the triphenyl-methane dyes, perpetuates the idea that reduction destroys colour. Scholl, however, pointed out (*Ber.* 1903, *36*, 3426; 1907, *40*, 934, 1691; 1908, *41*, 2304) that in some cases partial reduction causes deepening of colour; *e.g.* the reduction product indanthrene has a deeper colour than its oxidation product, anthraquinone-azine.



Anthraquinone-azine (greenish yellow).



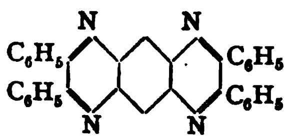
Indanthrene (blue).

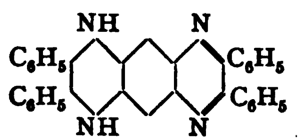
He explained this by pointing out that anthraquinone-azine

contains three chromophores, viz. two quinone chromophores and the azine chromophore, but no auxochromes. Reduction destroys the azine chromophore, but introduces two auxochromes, viz. the imino-groups. The two quinone auxochromes remain, and their effect is intensified by the auxochromes, which more than compensates for the loss of the azine chromophore.

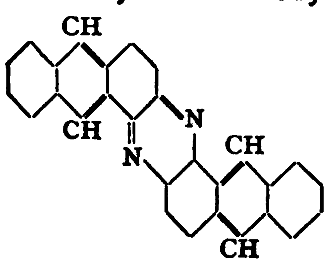
He enunciated the rule that "if chromogens which contain more than one chromophore are so reduced that one or more chromophores remain whilst the others are changed into auxochrome groups a deepening of colour may be produced." He gave the following further examples in illustration of his rule—

Nitroquinone (golden yellow);	Nitrohydroquinone (red);
1,2,Dihydroxydiquinoyl (rhodizonic acid), hydrate (colourless), salts (red);	Tetrahydroxyquinone (blue black); salts (black);
Naphthacenediquinone (leather brown);	Dihydroxynaphthacenequinone (ruby red);
Nitrophenazin (yellowish green);	Dinitrodihydrophenazin (blue violet), [mononitro compound unknown];
Tetraphenylbenzodipyrazin (yellow);	Tetraphenyldihydrobenzodipyrazin (blue).

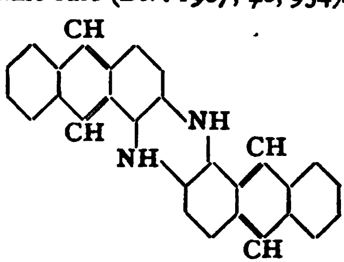




And he explained the change from yellow anthrazin to reddish brown dihydroanthrazin by the same rule (*Ber.* 1907, *40*, 934).



Anthrazin (yellow).

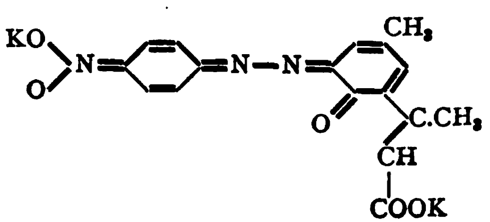


Dihydroanthrazin (reddish brown).

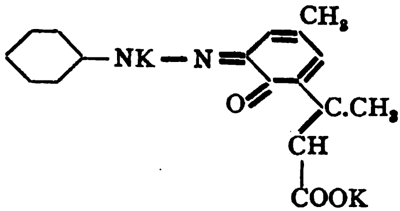
HEWITT'S RULE.—This investigator's researches on the colour of azo-compounds led him to the conclusion that the chief oscillation frequency is less, and consequently the colour is deeper, the longer the conjugate chain, *i.e.* the chain of alternate double and single bonds, in the molecule (*Chem. Soc. Trans.* 1907, *91*, 1251).

The observations which led him to formulate this rule were briefly as follows:—In the first place he was much impressed by the deep colour of the alkaline solutions of certain dyes which he happened to make, viz. *p*-nitrobenzene-azo-4:6-dimethylcoumarin (I) and *p*-nitrobenzene-azo-4-methyl-α-naphthacoumarin (II). The alkaline solutions of these substances are very much deeper in colour than those of the corresponding compounds without the nitro-groups, viz. benzene-azo-4:6-dimethylcoumarin (III) and benzene-azo-4-methyl-α-naphthacoumarin (IV). (*Chem. Soc. Trans.* 1906, *89*, 13, 17.) He noticed that a *p*-nitro-group in the nucleus not containing auxochromes generally produced this very pronounced deepening of colour in alkaline solution, *e.g.* *p*-nitrobenzene-azo-phenol (V) and *p*-nitrobenzene-azo naphthol (VI) have much deeper colours (crimson and violet) than benzene-azo-phenol (VII) (orange) and benzene-azo-naphthol (VIII) (crimson). He naturally concluded that the alkaline salts of these nitro-compounds had an essentially different structure from those of the non-nitrated compounds, and suggested that they were of the *iso*-nitroso form. The suggested formulæ for the compounds mentioned were as follows—

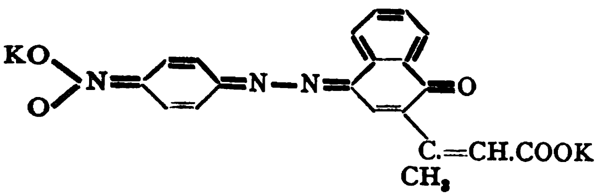
(I)



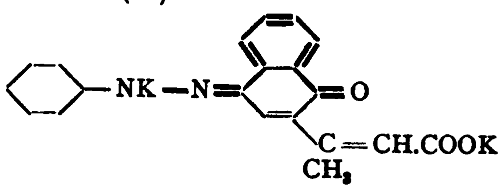
(III)



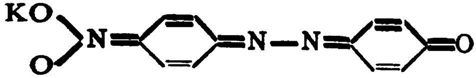
(II)



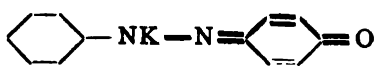
(IV)



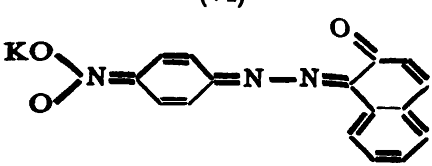
(V)



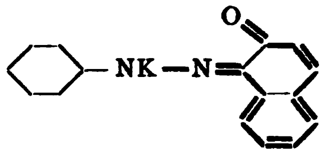
(VII)



(VI)

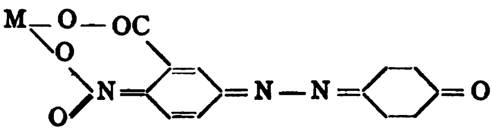


(VIII)

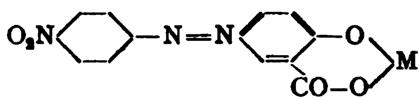


He found confirmation for these formulæ by preparing derivatives of these compounds (*a*) with a carboxyl group adjacent to the nitro group, (*b*) with a carboxyl group adjacent to the hydroxyl group. The salts of the heavy metals had the same deep colour in those cases where the carboxyl was adjacent to the nitro group, but not where it was adjacent to the hydroxyl. It may be fairly assumed that the heavy metal is held by adjacent hydroxyl and carboxyl groups, and this leads to the *iso*-nitroso formula for the deep-coloured salts with the heavy metals (IX), and where the formation

(IX)



(X)

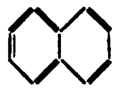


of the *iso*-nitroso salt is prevented the deep colour is not obtained (X). He felt that this justified assigning the *iso*-nitroso formula to the deep-coloured salts.

It will be noticed that in all cases the *iso*-nitroso formulæ contain a longer conjugate chain than do the formulæ of the corresponding compounds without the nitro-group. And it was on this evidence that Hewett suggested the rule with which his name is associated.

The present writer pointed out (*Chem. Soc. Trans.* 1914 *105*, *764*) that if Hewitt's rule is to be generally applicable

some further qualification must be demanded as to the conjugate chain, otherwise such compounds as naphthalene (XI),



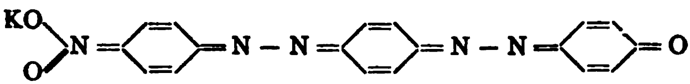
(XI)

which contains a fairly long conjugate chain, might be expected to be coloured.

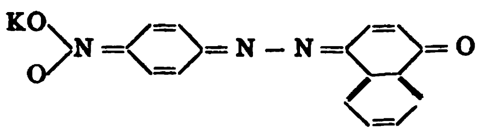
It was suggested (*loc. cit.*) that a further qualification should be required, viz. that the conjugate chain must be contained in a quinonoid formula, and Hewitt's rule so modified was suggested as generally applicable. The modified rule would run thus: "The chief oscillation frequency is less, and consequently the colour deeper, the longer the conjugate chain contained in the quinonoid formula of the substance."

Baly, Tuck and Marsden (*Chem. Soc. Trans.* 1910, *97*, 1494) threw doubt on the *iso*-nitroso formula suggested by Hewitt for the alkaline salts of the *p*-nitro-azo-compounds; and Sircar (*Chem. Soc. Trans.* 1916, *109*, 757 *et seq.*) came to the conclusion that Hewitt's rule must be modified for the azo-series, the depth of colour being proportional to the length of the conjugate chain in the part of the molecule containing the auxochrome, counting from the auxochrome to the azo-linking.

Sircar noticed that *p*-nitrobenzeneazobenzeneazophenol (XII) dissolved in alkali with a lighter colour (purple) than *p*-nitrobenzene-1-azo-4-naphthol (blue) (XIII), although in the *iso*-nitroso form it has a longer conjugate chain than the latter.

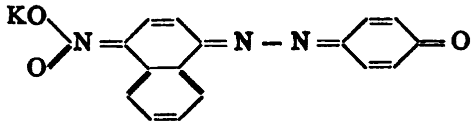


(XII)



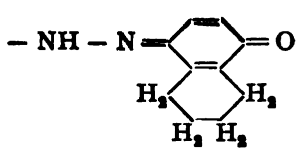
(XIII)

He prepared 4-nitronaphthalene-1-azophenol (XIV), and compared it with *p*-nitrobenzene-1-azo-4-naphthol (XIII). In the *iso*-nitroso form these substances would contain conjugate chains of the same length,

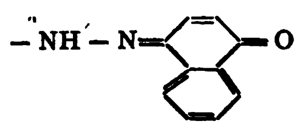


(XIV)

but the alkaline solution of the former is red, whilst that of the latter is blue. Hence he concluded that the colour of azo-compounds could not be estimated by the length of the conjugate chain reckoned in the way suggested by Hewitt. But he brought forward a considerable amount of evidence to show that the colour is proportional to the length of the conjugate chain in the part of the molecule containing the auxochrome, *e.g.* dyes formed by coupling diazo-compounds with tetrahydronaphthol have only a light colour. The hydrogenation of the naphthalene nucleus has shortened the conjugate chain (XV). Compare with the non-hydrogenated nucleus (XVI)—

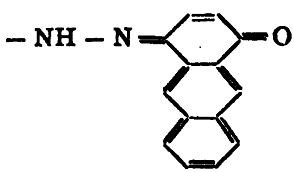


(XV)



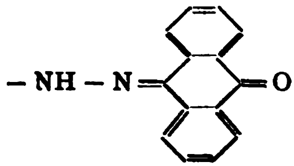
(XVI)

Dyes formed from α-anthrol (XVII) have a longer conjugate than those from α-naphthol (XVI), and they have a deeper colour—



(XVII)

The isomeric compounds from anthranol have shorter conjugate chains (XVIII) than those from α-anthrol, and they also have a lighter colour—

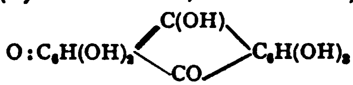


WATSON'S RULE.—The present writer pointed out (*Proc. Chem. Soc.* 1913, *29*, 348; *Chem. Soc. Trans.* 1914, *105*, 759) that dyes which are quinonoid in all possible tautomeric forms have a deep colour, no matter how simple their structure or how small their molecular weight.

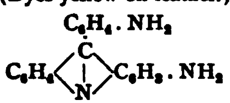
"In the following table there are placed opposite each other in the two columns dyes of very similar constitution which yet show remarkable differences in depth of colour—

Hexahydroxybenzophenone
(Dyes yellow on alum and chrome.)
$C_6H_2(OH)_3 . CO . C_6H_2(OH)_3$

Anthracene blue W.R.
(Dyes violet on alum, blue on chrome.)



Leather yellow
(Dyes yellow on leather.)

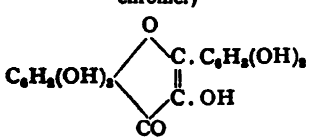


Magenta
(Dyes bluish red.)
$C_6H_4 . NH_2$
$ClH_2N : C_6H_4 : \dot{C} . C_6H_4 . NH_2$

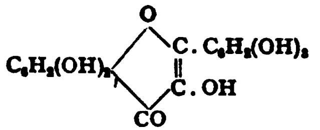
4:4'-Diaminoazobenzene
(Yellow)
$NH_2 . C_6H_4 . N : N . C_6H_4 . NH_2$

Indamine
(Blue
$NH : C_6H_4 : N . C_6H_4 . NH_2$

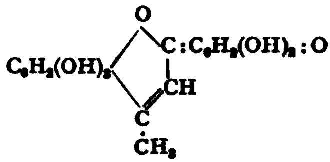
Quercetin
(Yellow on alum, yellowish brown on chrome.)



Myricetin
(Dyes similar shades to quercetin.)



Gallacetein
(Dyes violet on chrome.)



"The dyes in the right-hand column can only be represented by formulæ containing a quinonoid arrangement. Whatever tautomeric change they may be supposed to undergo their formulæ still contain the quinonoid arrangement. Those on the left-hand differ in that they can be represented by formulæ not containing this arrangement. They can, of course, be supposed to tautomerise into forms containing this quinonoid arrangement, but in all cases it is possible to represent them also in a non-quinonoid form."

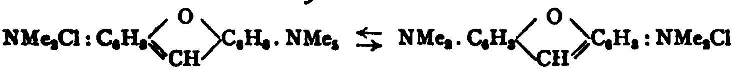
"A survey of all the better known dye-stuffs fully bears out this theory. The triphenylmethane dyes, the pyronines, benzeïns and fluorones, the indophenols, indamines, oxazines, thiazines, azines (safranines, etc.), all satisfy this requirement and exhibit deep colour, in many cases with little molecular complexity. Hæmateïn and brazileïn conform to this rule. They have almost the same molecular weight as the flavones, and there is considerable resemblance in their structure; but they conform to this rule, whilst the flavones do not, and consequently their colour is much deeper. The alizarin series, and also naphthazarin, illustrate the rule. On the other hand the monoketonic dyes, *e.g.* the benzophenone and xanthone derivatives, the flavones and flavonols, ellagic acid and the azo-dyes can be represented by non-quinonoid formulæ; and many members of these groups, despite very considerable molecular complexity, have no great depth of colour. The following formulæ show the different possible tautomeric forms of typical dyes of these groups which illustrate this difference.

Magenta

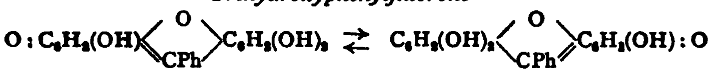
$$\begin{array}{c} C_6H_4 . NH_2 \\ NH_2Cl : C_6H_4 : \dot{C} . C_6H_4 . NH_2 \end{array} \rightleftarrows \begin{array}{c} C_6H_4 : NH_2Cl \\ NH_2 . C_6H_4 . \ddot{C} . C_6H_4 . NH_2 \end{array} \rightleftarrows$$

$$\begin{array}{c} C_6H_4 . NH_2 \\ NH_2 . C_6H_4 . \dot{C} : C_6H_4 : NH_2Cl \end{array}$$

Pyronine G



Trihydroxyphenylfluorone



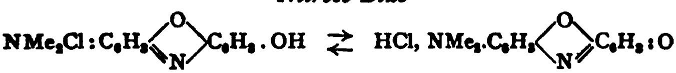
Indophenol

$$O : C_{10}H_6 : N . C_6H_4 . NMe_2, HCl \rightleftarrows HO . C_{10}H_6 . N : C_6H_4 : NMe_2Cl$$

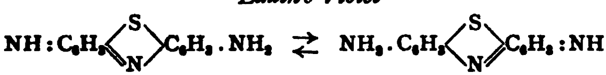
Phenylene Blue

$$NH : C_6H_4 : N . C_6H_4 . NH_2 \leftrightarrows NH_2 . C_6H_4 . N : C_6H_4 : NH$$

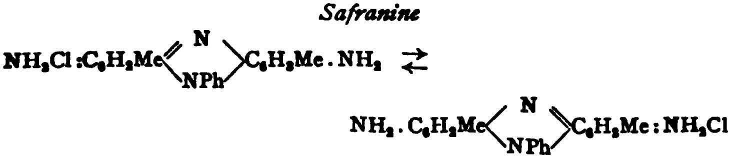
Nitroso Blue



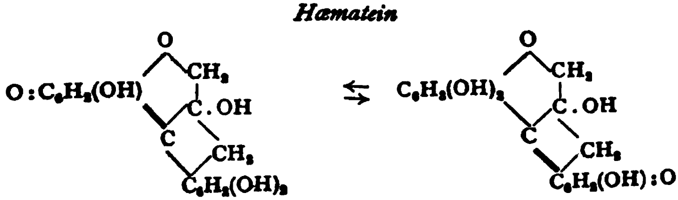
Lauth's Violet



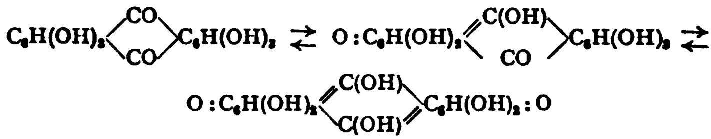
Safranine



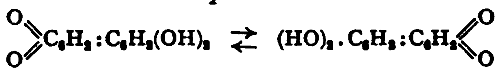
Hæmatein



Anthracene Blue WR



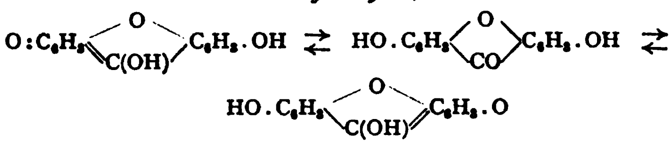
Naphthazarin



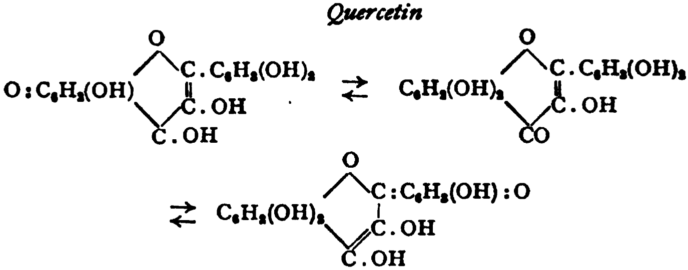
Hexahydroxybenzophenone

$$O:C_6H_2(OH)_2:C(OH).C_6H_2(OH)_3 \rightleftarrows C_6H_2(OH)_3.CO.C_6H_2(OH)_3 \rightleftarrows$$
$$C_6H_2(OH)_3.C(OH):C_6H_2(OH)_2:O$$

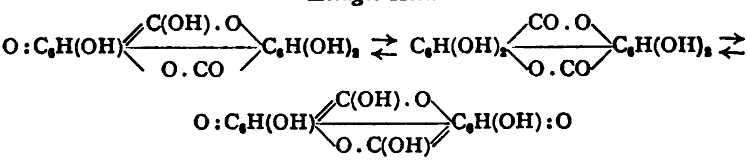
Dihydroxyxanthone



Quercetin



Ellagic Acid

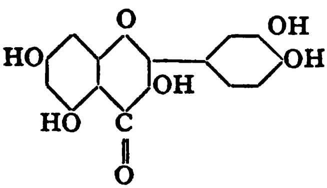


Benzeneazophenol

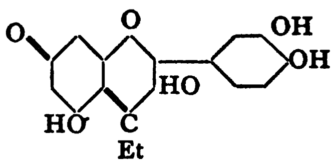
$$C_6H_5.NH.N:C_6H_4\ O \rightleftarrows C_6H_5.N:N.C_6H_4.OH$$

This theory was tested by starting from quercetin, which has only a light colour (yellow in alkaline solution), and the

formula for which can be written in a non-quinonoid form (XIX). By a series of chemical operations its structure was slightly altered so that it was rendered permanently quinonoid (XX). The new substance produced could tautomerise from one quinonoid form to another, but could not assume a non-quinonoid form. And, as expected from the theory, this new substance had a deep colour. It dissolved in alkalies with a blue colour.



(XIX)

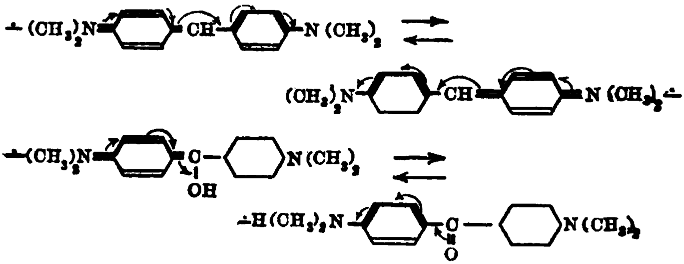


(XX)

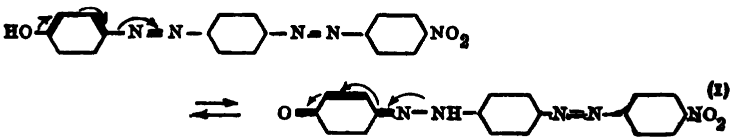
WATSON'S AND MEEK'S MODIFICATION OF HEWITT'S RULE.—In passing from one tautomeric form to another there is a reversal of the conjugate chain, so that double and single bonds change places all along the conjugate chain. In that group of substances which can only tautomerise from one quinonoid form to another the conjugate chain reversed is generally longer than in the other group of substances which can tautomerise from a quinonoid to a non-quinonoid form. An appreciation of this fact led to the formulation of a further modification of Hewitt's rule, viz. that the colour is deeper the longer the conjugate chain reversed during tautomeric change (Watson and Meek, *Chem. Soc. Trans.* 1915, *107*, 1567). This rule was tested by measuring the wave-lengths of the maxima of the absorption bands of seven pairs of substances which were selected as being very similar in structure, but having conjugate chains of different lengths reversed during tautomerism. It was found that in each of these seven pairs the period of the vibration was proportional to the length of the conjugate chain reversed.

	Length of conjugate chain reversed during tautomerism.	Wave-length of absorption band.
$\frac{\text{4:4'-Tetramethyldiaminobenzhydrol}}{\text{4:4'-Tetramethyldiaminobenzophenone}}$	$\frac{5}{3}$ ratio $= 1\cdot\dot{6}$	$\frac{6100}{3680}$ ratio $= 1\cdot65$
$\frac{\text{4:4'-Diaminobenzhydrol}}{\text{4:4'-Diaminobenzophenone}}$	$\frac{5}{3}$ ratio $= 1\cdot\dot{6}$	$\frac{5640}{3414}$ ratio $= 1\cdot65$
$\frac{\text{Quercetin reduction product}}{\text{Quercetin}}$	$\frac{5}{3}$ ratio $= 1\cdot\dot{6}$	$\frac{6100}{3690}$ ratio $= 1\cdot65$
$\frac{\text{Morin reduction product}}{\text{Morin}}$	$\frac{5}{3}$ ratio $= 1\cdot\dot{6}$	$\frac{5860}{3800(?)}$ ratio $= 1\cdot54$(?)
$\frac{\text{Apigenin reduction product}}{\text{Apigenin}}$	$\frac{5}{3}$ ratio $= 1\cdot\dot{6}$	$\frac{5700}{3410}$ ratio $= 1\cdot67$
$\frac{\text{Pyronine G}}{\text{3.6. Tetramethyldiaminoxanthone}}$ . .	$\frac{4}{3}$ ratio $= 1\cdot\dot{3}$	$\frac{5480}{3861}$ ratio $= 1\cdot41$
$\frac{\text{3. Hydroxyfluorone}}{\text{3.6. Dihydroxyxanthone}}$	$\frac{4}{3}$ ratio $= 1\cdot\dot{3}$	$\frac{5040}{3810}$ ratio $= 1\cdot32$

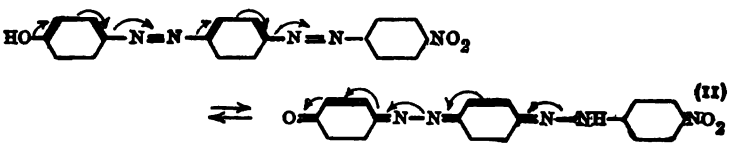
The reversal of the chain is shown in the following structural formulæ for 4:4'-tetramethyldiaminobenzhydrol (Michler's hydrol) and 4:4'-tetramethyldiaminobenzophenone (Michler's ketone).



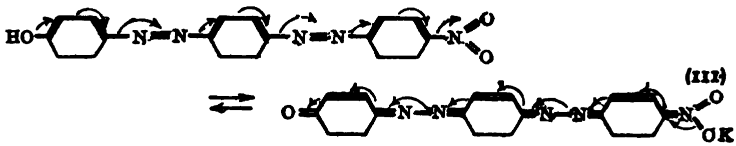
It should be pointed out, however, that for some compounds more than two tautomeric forms are theoretically possible, and in some cases the length of the conjugate chain reversed is different according as we consider the change from (say) the first tautomeric form to the second, or from the first to the third, *e.g.* in the case of *p*-nitrobenzeneazobenzeneazophenol there are three possible quinonoid forms, and the length of chain reversed in passing from the non-quinonoid form to each of these is different.



(I)



(II)



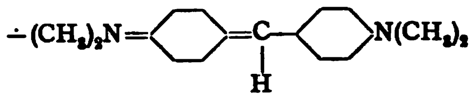
(III)

Sircar's work has shown that the colour does not always correspond to the reversal of the longest possible conjugate chain, and chemical evidence cannot be relied on to tell us definitely which change will actually take place, so that the theory cannot always tell us definitely what colour we may expect.

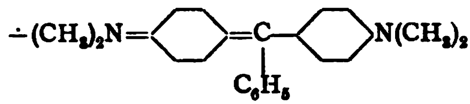
It must also be admitted that in some cases deep colour is developed when there is no long conjugate chain to be reversed, *e.g.*, in the case of the tertiary fatty nitroso compounds. It can only be suggested that in all ordinary dyes the colour is due to the periodic reversal of a conjugate chain of considerable length, but in some special cases the colour may be due to an entirely different kind of vibration.

It must also be clearly pointed out that other factors, besides the length of conjugate chain reversed during tautomerism, affect the depth of colour, and it is only when comparing substances of very similar constitution that we find the wave-lengths of the maxima of the absorption bands exactly proportional to the lengths of the conjugate chains reversed during tautomerism. In the first place the vibration can be made slower by weighting the molecule, even when the length of conjugate chain is unaltered, *e.g.* by brominating fluoresceïn we obtain eosin, which has a considerably

deeper colour, although the length of conjugate chain is unaltered. We see the same effect by comparing Michler's hydrol (XXI) and malachite green (XXII); the replacement of the methane hydrogen atom by a phenyl group deepens the colour from blue to green.



(XXI)



(XXII)

We may find an analogy for this in the vibration of stretched strings. For strings of the same material and under the same tension the period of vibration is proportional to the length, but if we take two exactly similar strings and affix a weight to one of them the periods of vibration will no longer be the same—the loaded string will vibrate more slowly.

Again, we have already drawn attention to the very special effect of additional auxochromes in deepening colour. This cannot be explained as due to the weight of the additional auxochromes, because other atoms or groups of equal or greater weight introduced into the molecule instead of the additional auxochromes do not produce nearly so great an effect on the colour, *e.g.* the bromine and ethoxy-derivatives of alizarin have not such deep colours as the polyhydroxy-anthraquinones. Nor in most cases do the additional auxochromes lengthen the conjugate chains which can reverse.

A very special effect is produced by modification of the auxochromes at the ends of the conjugate chain, as, *e.g.*, by alkylating or arylating the amino-groups of fuchsin or *p*-rosaniline, or, in the case of mordant dyes, by combination with different metals. In many cases the colour is so different on different mordants that such dyes have been

termed polygenetic, Logwood, alizarin, fustic, and cochineal may be given as examples of polygenetic dyes. Alizarin is yellow in alcoholic solution, gives orange dyeings on tin, red on alum, maroon on tin, and is purple in alkaline solutions. An exactly similar case is that of violuric acid with its different coloured salts. As we have already seen, the regular deepening of colour produced in the triphenylmethane group by the systematic alkylation or arylation of the amino groups has been attributed to the weight of the added alkyl or aryl groups. But in the case of the mordant dyes the depth of colour attained does not depend on the weight of the metal with which the dye has formed a salt, but rather on the electropositivity of the metal: the colour is deeper the more electropositive the metal. The order is tin, alum, chrome, and sodium or potassium, so that it very obviously does not depend on the weight of the metal (Meek and Watson, *Chem. Soc. Trans.* 1916, *109*, 554). Hantzsch found that the depth of colour of the violurates, diphenylviolurates, isoxazolone salts, etc., was also proportional to the electro-positivity of the combined metal. Meek and Watson (*loc. cit.*) offered the following explanation of this phenomenon: "If we consider these conjugate chains as in a state of tension, the period of oscillation will be shorter the greater the tension, and the tension will be the greater the more firmly the metallic radicle is combined with the dye. When the dye is combined with a strong positive radicle the degree of dissociation in solution will be greater than when it is combined with a weak positive radicle. In a partly dissociated compound some molecules have still the metallic radicle attached to the dye molecule. The greater the dissociation the smaller is the number of molecules which have still the attached metallic radicle. We may regard the electric tubes of force from the metallic atom as partly connecting with the dye molecule and partly radiating around. The larger the dissociation, the smaller will be the number of tubes of force joining the metallic radicle to the dye molecule in those molecules which are undissociated, and the smaller will be the tension in the chain, and therefore the longer will be

the wave-length of the maximum of the absorption band. Hence by increasing the positive nature of the radicle, the absorption band should be moved towards the red end of the spectrum."

Some work which has been done on the lakes of *alkanna* has reference to the change of colour, or, more precisely, the shifting of the absorption bands of certain organic dye-stuffs on combining them with different metals. Vogel and v. Lepel made some observations on the subject, and Formanek (*Z. f. anal. Chemie*, 1900, *31*, 409–434, 673–693; *Qualitative Spectralanalyse anorganischer Körper*, Mückenberger, Berlin, 1900) studied the lakes of alkanna very minutely. The characteristic absorption bands are observed in an alcoholic solution of alkanna to which a metallic chloride has been added. In some cases it is also necessary to add a trace of ammonia. Three sharp absorption bands are observed, and the positions of these bands are different for different metals. Formanek claimed that you could identify a metal by adding its chloride to alkanna solution and measuring the positions of the absorption bands. He has recorded the positions of these bands for the alkanna lakes of many metals. And for the lakes of the alkali metals and alkaline earths his work has been repeated by Laubenthal (*Drudes Ann.*, 1902, *7*, 851–861) using a spectrophotometric method for determining the positions of the absorption maxima.

Formanek's results are inserted for convenience in a periodic arrangement of the elements. The wave-lengths of the maxima of the first absorption band of the lakes are given. The same regularities would be observed for the second and third absorption bands.

	I	II	III	IV	V	VI	VII	VIII
1	H							
2	Li 6210	Be 5820	B	C	N	O	F	
3	Na 6337	Mg 6064	Al 5857	Si	P	S	Cl	
4	K 6387	Ca 6147	Sc	Ti 6271	V 6099	Cr	Mn 6171	Fe Ni Co 6545 6192 6370 5895 6198 6354
5	Cu 5953 5945	Zn 6016	Ga	Ge	As	Se	Br	
6	Rb 6397	Sr 6223	Y 6021 6016	Zr 6030	Nb	Mo 5845		Rh Ru Pd 6418 6084
7	Ag	Cd	In 5961	Sn	Sb	Te	I	
8	Cs 6410	Ba 6281	La 6120	Ce 6115 6123	Di			
9								
10					Ta	W		Os Ir Pt
11	Au	Hg	Tl 6288	Pb	Bi			
12				Th 6070		U 6870		

It will be noticed that for the alkali metals increase of atomic weight causes an increase in the wave-length of the maximum of the absorption band; and the same is true for the alkaline earths. This regularity is confirmed by Laubenthal's figures:—

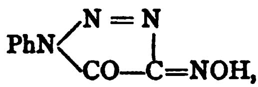
Metal.	Frequency of maximum of absorption band.	Metal.	Frequency of maximum of absorption band.
Li . . .	1604	Mg . . .	1648
Na . . .	1578	Ca . . .	1624
K . . .	1559	Sr . . .	1606
Rb . . .	1556	Ba . . .	1590
Cs . . .	1553		

It will be observed, however, that this relation between atomic weight and vibration frequency only holds for particular groups, and that there is generally a decrease of wave-length with increase of atomic weight if we examine the elements in series rather than in groups.

The conclusion arrived at by Meek and Watson (*loc. cit.*), viz. that the colour is deeper the more electropositive the metal, was based on a very limited number of observations, and under somewhat different conditions from those of Formanek and Laubenthal. The absorption maxima for alizarin, etc., occupy the same positions whether the dyes are dissolved in soda or potash, probably because the salts are completely ionised under these conditions. Different results might be obtained in alcoholic solution, so that this work is not necessarily in disagreement with the earlier work of Formanek and Laubenthal.

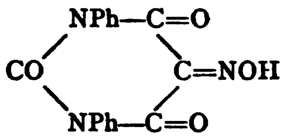
Hantzsch's Theory of Chromo-Isomerism

Hantzsch has offered a different explanation of the range of colours exhibited by diphenylvioluric acid and other polygenetic acids when combined as salts with different metals, and at this point we may give a short account of his work on *chromo-isomerism*, as he termed this phenomenon. Since 1907 he has shown that many coloured organic compounds can exist in several different coloured forms, *e.g.* he has isolated yellow, red, green and violet potassium salts of *p*-nitrophenylnitromethane; yellow, red and green salts of 4-oximino-1-phenyl-5-triazolone—

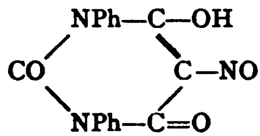


orange and violet salts of aminoazobenzene, aminoazobenzene sulphonic acid and dimethylaminoazobenzene sulphonic acid (Helianthin); red, violet and blue violurates; green and red modifications of azophenol; yellow, red and green modifications of azophenol salts and a large number of isomeric phenylacridonium and phenylmethylacridonium salts. It is

natural to suppose that differently coloured forms of the same substance, or, in other words, substances which have different colours but the same chemical deportment, may be polymers. The red and yellow forms of mercuric iodide are so explained. But Hantzsch showed that many of the chromo-isomers which he studied had the same molecular weight, and the explanation of their different colours had to be sought in some other direction. It was possible to imagine different tautomeric forms for many, if not all, of these substances, *e.g.* for diphenylvioluric acid we can easily imagine the two forms XXIII and XXIV—



(XXIII)



(XXIV)

Hantzsch regarded it as axiomatic that each form would have its characteristic absorption spectrum and colour—in other words, that there would be a definite absorption spectrum corresponding with each modification of constitutional formula. And in some cases he was able to imagine or devise as many modifications of the constitutional formula as he had succeeded in isolating chromo-isomeric forms. But in other cases it was beyond the power of his imagination to devise sufficient formulæ for all the different coloured forms. In these cases he assumed that there was a different colour corresponding with each formula, and the remaining coloured forms to which no separate formulæ could be assigned were regarded as mixtures, mixed crystals in the case of crystalline solids, or solutions containing two or more forms if it was only a case of explaining colours in solution. In the case of the diphenylviolurates he could only imagine the two formulæ already given, one nitroso-enolic and the other oximino-ketonic. To the one form he assigned an absorption band at frequency 1500, and to the other a band at 3800. Now the cæsium salt in acetone solution has a band with its maximum at 1700, the lithium salt in acetone

has maximum absorption at 1950, and the same salt in ethyl acetate has maximum absorption at 3250. Other salts under various conditions have bands lying between 1500 and 3800. If Hantzsch's theory is correct, these bands at 1700, 1950, 3250, and so on, are the resultants of bands at 1500 and 3800. Now it is true that suitable bands at 1500 and 3800

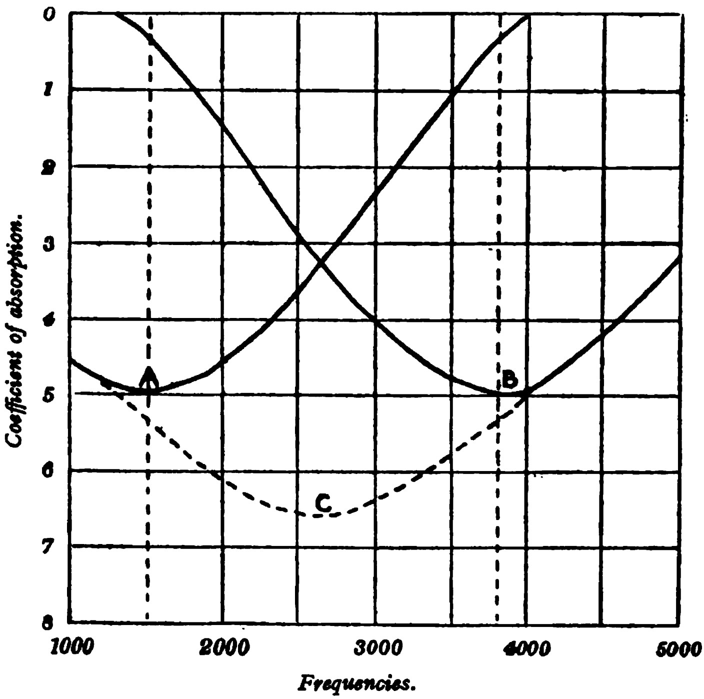


FIG. 54.

(Reproduced from Russell and Lapraik's paper, *Chem. Soc. Trans.*, 1881, 39, pp. 168 *et seq.*, Plate.)

can be compounded to give bands at these intermediate positions. Let A and B in Fig 54 represent the absorption curves of two substances which have maxima of absorption at 1500 and 3800 respectively.

A solution containing these two substances in equal amounts would have an absorption compounded of the two, and shown in the same figure by the curve C, which has maxi-

mum absorption at about 2800. A solution containing twice as much of A as of B would give a maximum nearer to 1500 as shown in Fig. 55, and it is obvious that by taking A and B in suitable proportions we could get maximum absorption at 1700, 1950, and 3250 respectively. It is found that by taking A and B in the proportion 10 : 5, 10 : 8, and 8 : 10 this can be

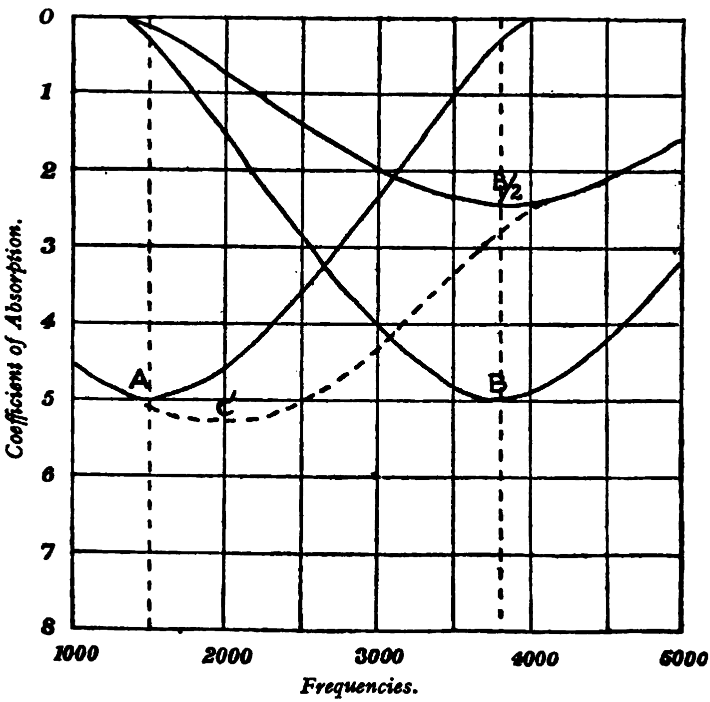


FIG. 55.

done, and the resultant absorption curves are shown in Fig. 56. But it should be noted that this can only be done if the absorption bands are very broad, when the compounded absorption bands will also be very broad. If the absorption bands of the two fundamental substances are narrower, as in Fig. 57, it will be seen that in whatever proportion the two substances are mixed we cannot get rid of maxima of absorption at 1500 and 3800.

H

Now Hantzsch has recorded the absorption curves of the diphenylviolurates, and we are able to compare them with the curves which have been compounded (Fig. 58).

It is at once obvious that there is no resemblance between

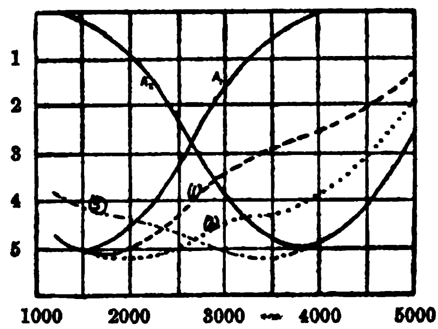


Fig. 56.

—— A_1 and A_2 are two fundamental bands at frequencies 1500 and 3800.
(1) - - - - Resultant of A_1 and A_2 in the ratio of 10 : 5.
(2) . . . . . „ „ „ „ 10 : 8.
(3) —— „ „ „ „ 8 : 10.

(Reproduced from Meek and Watson's paper, *Chem. Soc. Trans.*, 1916, 109, p. 552, Fig. 9.)

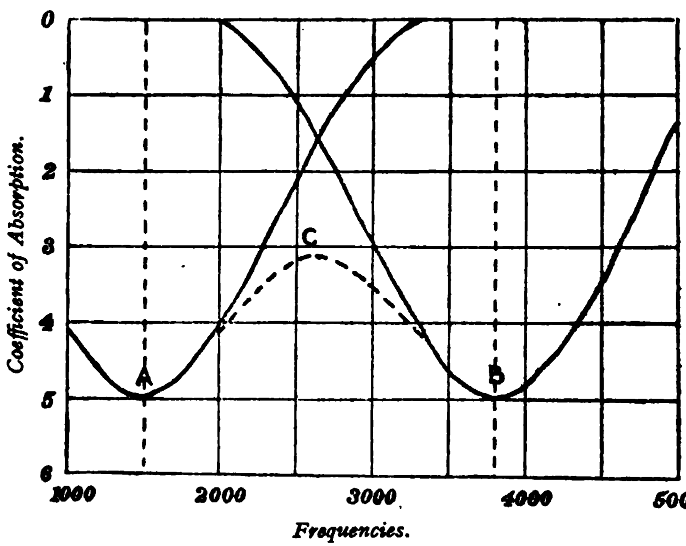


Fig. 57.

the experimental and synthetic curves. The synthetic curves are very much broader, and the minimum of absorption at 2400 is entirely absent. Yet it is impossible to get narrower absorption bands at 1700, 1950 and 3250 by compounding any kind of bands at 1500 and 3800. In fact the experimental curves recorded by Hantzsch render his hypothesis

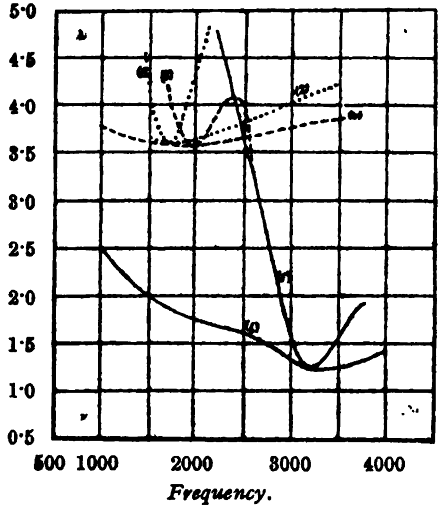


FIG. 58.

(1) (3) (5) are Hantzsch's curves for diphenyl violuric acid (*Ber.*, 1910, 43, 666).
(1) Cs salt in acetone solution.
(3) Li salt in acetone solution.
(5) Li salt in ethyl acetate solution.
(2) (4) and (6) are curves compounded from the fundamental bands at 1500 and 3800, so that the maxima of the resultant curves correspond with those of Hantzsch's three curves.

(Reproduced from Meek and Watson's paper, *Chem. Soc. Trans.*, 1916, 109, p. 553, Fig. 10.)

untenable. Such curves cannot be resolved into bands at 1500 and 3800.

EFFECT OF MULTIPLICATION OF AUXOCHROMES ON DEPTH OF COLOUR

It has already been mentioned several times that additional auxochromes have a specially great effect on the depth of colour, and some examples have been given in a table in Chapter I.

At first sight it appears as though additional auxochromes have a much greater effect in some groups of dyes than in others, *e.g.* additional auxochromes are able to change the colour from red to blue in the polyhydroxyanthraquinone series, and from yellow to blue in the phthaleïn series; whilst in the hydroxybenzophenone and flavone groups we are unable to get beyond yellow or brown shades however many auxochromes are introduced. But, as the present writer has pointed out (Perkin and Watson, *Chem. Soc. Trans.* 1915, *107*, 198), this difference may be more apparent than real. A comparatively small shift of an absorption band in the green, yellow, or orange part of the spectrum produces a marked difference in the colour of the transmitted light; whilst an equal shift of a band in the blue or violet part of the spectrum has very little effect on the colour as seen by the unaided eye.

The relative position of the auxochromes has a very great effect on the colour, *e.g.* there are two isomeric hexahydroxyanthraquinones, viz., Anthracene Blue WR and rufigallol, one one of which is blue and the other brown.

The polyhydroxyanthraquinone group provides a very convenient illustration of the way in which the colour depends not only on the number of the auxochromes, but also on their positions in the molecule, and it is instructive to tabulate the available data for this group (pp. 102, 103).

Several investigators have attempted to deduce rules as to the relation between the positions of the auxochromes and the colour developed in this group. The general impression is, that it is necessary to have at least two auxochromes in the *ortho*-position to one another, and also adjacent to a carboxyl group (as in alizarin), in order to get a deep colour developed. This impression has almost certainly come from Liebermann and Kostanecki's work (*Ber.* 1885, *18*, 2145), but is not justified, as a reference to the original paper will show. These investigators did not concern themselves with the colour of the polyhydroxyanthraquinones, but with their dyeing properties, *i.e.* with their power to affix themselves to the oxides of aluminium, iron, chromium, or tin, on the textile fibres (as they are not direct, but mordant dyes).

Georgievics (*Monatsch*, 1911, *32*, 329 *et seq.*) considered the colours of the lakes, and came to the conclusion that α-hydroxyls tended to produce red and blue colours, whilst β-hydroxyls tended to produce yellow or brown colours. But this generalisation needed some interpretation. In his own words: "Hydroxyl groups in the α-position produce red and blue dyes, in the β-position yellow and brown dyes; however, an α-hydroxyl group may mask the effect of a β-hydroxyl group, and *vice versa*. . . . The hydroxyanthraquinones, therefore, are divisible into two groups: one group . . . forming yellow and brown lakes, has a para-quinonoid structure, for example, anthragallol . . . whilst the other group, which includes alizarin and its derivatives, forming red or blue lakes (except hystazarin, which occupies an intermediate position), has an ortho-quinonoid structure. . . . In individual hydroxyanthraquinones the tendency to the production of one or other of the quinonoid forms may be such that one and the same dye may be ortho-quinonoid in some lakes and para-quinonoid in others."

The present writer, in conjunction with his colleague Prof. Meek, has criticised Georgievics' generalisations and suggested others which seem to him more in harmony with the facts, and which seem applicable, not only to the polyhydroxyanthraquinones, but to all groups of dyes (Meek and Watson, *Chem. Soc. Trans.* 1916, *109*, 557 *et seq.*).

"These generalisations seem open to criticism on the following grounds—

(1) They do not explain why two hydroxyl groups at least are necessary to produce a red or a blue colour. It may be said that the monohydroxy-derivatives are not mordant dyes, and are therefore not included in the generalisations about lakes. We have shown above, however, that there is a simple relationship between the colour of a dye in alkaline solution and on the various mordants, and consequently Georgievics' generalisations should hold also for the colour of the alkaline solutions of the dyes. From his rules we might expect that 1-hydroxyanthraquinone would have a red or a blue colour, but, as a matter of fact, in alkaline solution it has an absorption band at $\lambda = 4960$, and

Anthraquinone derivative.	Shade of dyeing on Tin.	Shade of dyeing on Alum.	Shade of dyeing on Chrome.	Colour of K or Na Salt.	Colour of Ca Salt.	Colour of Ba Salt.	
1 monohydroxy							
2 monohydroxy				reddish yellow		(1) yellow (2) red	
1.2 dihydroxy	orange	red	maroon	violet	purple	blue	
1.3 dihydroxy		dull orange	yellowish brown	red	red brown		
1.4 dihydroxy	orange	red	maroon	blue		bluish violet	
1.5 dihydroxy				reddish violet	carmine red	carmine red	
2.3 dihydroxy	orange	dull red	bordeaux	cornflower blue	dark violet	dark blue	
2.7 dihydroxy				red			
1.2.3 trihydroxy	brownish orange	brown	brown	brown green?		black	Pb. violet brown
1.2.4 trihydroxy	reddish orange	red	magenta	red	purple red	purple red	Pb. violet
1.2.5 trihydroxy	similar to alizarin, but somewhat bluer shades			cornflower blue		blue	
1.2.6 trihydroxy	similar to alizarin, but somewhat yellower shades			purple		red violet	
1.2.7 trihydroxy	similar to alizarin, but somewhat yellower shades			violet		violet	
1.2.8 trihydroxy	similar to alizarin, but somewhat browner shades						
1.4.5 trihydroxy	poor red	poor red	dull greyish blue				
1.2.3.4 tetrahydroxy		dirty red		red			

1.2.3 (5 or 7) tetrahydroxy	brownish orange	brown	brown	emerald green			
1.2.3 (7 or 5) tetrahydroxy	brownish orange	brown	brown	emerald green			
1.2.5.6 tetrahydroxy . .	similar to alizarin, but somewhat bluer shades						
1.2.7.8 tetrahydroxy . .	similar to alizarin, but somewhat browner shades						
1.2.5.8 tetrahydroxy . .	red	bordeaux	bordeaux				
1.4.5.8 tetrahydroxy . .			blue				
1.3.5.7 tetrahydroxy . .	dull orange		yellowish brown				dark red
1.2.4.6 tetrahydroxy . .	identical with 1.2.4						
1.2.4.7 tetrahydroxy . .	similar to 1.2.4 but a little bluer						
1.2.4.8 tetrahydroxy . .	similar to 1.2.4 but a little bluer						
1.2.4.5.8 pentahydroxy .	bordeaux	violet	blue	blue			
1.2.3.5.7 pentahydroxy .	brownish orange	brown	brown	brownish yellow in dilute NaOH, green in strong			
1.2.3.5.6.7 hexahydroxy .	brownish orange	brown	brown	violet with dilute KOH indigo blue with strong		blue	
1.2.4.5.6.8 hexahydroxy .	bordeaux	violet	blue	blue			
1.2.3.4.5.6.7.8 octahydroxy	red	reddish blue	reddish violet				

the colour of the solution is yellow. Alizarin (1:2-dihydroxyanthraquinone), according to his rules, should have the blue colour due to the hydroxyl in the α-position partly masked by the yellow of the hydroxyl in the β-position, but, as is well known, alizarin dissolves in potassium hydroxide with a bluish-violet colour.

(2) They do not explain why 1:4-dihydroxyanthraquinone should have a deeper colour than 1:5- or 1:8-dihydroxyanthraquinone. Quinizarin (1:4-dihydroxyanthraquinone) is blue in potassium hydroxide solution, and has a blue violet barium salt; anthrarufin (1:5-dihydroxyanthraquinone) is reddish violet in potassium hydroxide, and has a carmine red barium salt; chrysazin (1:8-dihydroxyanthraquinone) is yellow red in potassium hydroxide, and has a red barium salt.

(3) They do not explain why alizarin should have as deep a colour as quinizarin. According to these rules the β-hydroxyl should have a prejudicial effect.

(4) They do not explain why alizarin should have a much deeper colour than 1:3-dihydroxyanthraquinone.

(5) They do not explain the deep colour of 2:3-dihydroxyanthraquinone, namely, cornflower blue in potassium hydroxide, red on alum mordant; the calcium salt is violet, and the barium salt blue.

These criticisms suggest a generalisation which seems much more in harmony with the facts than those of Georgievics, namely—

(*a*) Two hydroxyl groups in one benzene nucleus in the ortho- or para-position with respect to one another are necessary to produce a deep (red, violet, or blue) colour.

(*b*) The colour is still further deepened if both benzene nuclei contain pairs of hydroxyl groups in the *o*- or *p*-position to one another.

(*c*) Three hydroxyl groups in the 1:2:4-positions in one benzene nucleus produce a deeper colour than a pair of hydroxyl groups in the *o*- or *p*-position.

(*d*) Three hydroxyl groups in the 1:2:3-positions in one benzene nucleus produce a brown colour.

The generalisations bear a marked resemblance to the rules put forward by Kauffmann (Kauffmann and Franck,

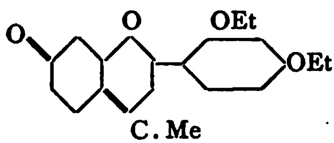
Ber., 1906, *39*, 2722), and are probably applicable to all groups of dyes, for example—

(*a*) The hydroxy-derivatives of azobenzene dissolve in potassium hydroxide with the following colours:

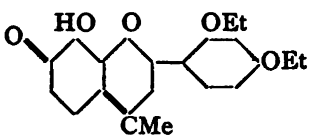
p-Hydroxyazobenzene . . .	yellow.
o-hydroxyazobenzene . . .	yellow.
Benzeneazoresorcinol . . .	orange.
Benzeneazocatechol	carmine.
Benzeneazoquinol	blue.
Benzeneazopyrogallol . . .	brick-red.

(*b*) Fluorescein, quinolphthalein, and catecholphthalein dissolve in potassium hydroxide with a yellow colour; hydroxyquinolphthalein gives a cherry-red, gallein a blue, and phloroglucinolphthalein an orange under the same conditions.

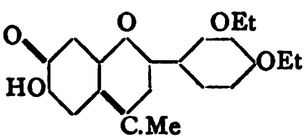
(*c*) In the pyranol system of dyes (prepared partly by Bülow and partly by Watson and Sen) the effect of two hydroxyl groups in the ortho-position with respect to one another can be seen from the following comparison—

(1) 

Gives redder and yellower dyeings than alizarin brown.

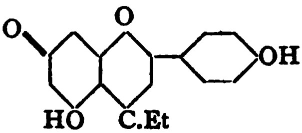
(2) 

Green with sodium alkyloxide, blue in pyridine. Olive green dyeings on chrome.

(3) 

Dark red with alcoholic potassium hydroxide.

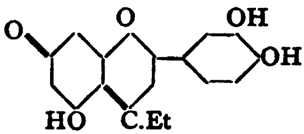
The less favourable effect, so far as depth of colour is concerned, of two hydroxyl groups in the *m*-position with respect to one another in the benzo-group can be seen by comparing the preceding with

(4) 

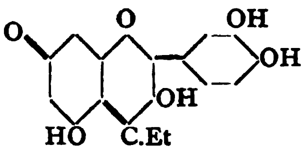
Crimson with potassium hydroxide, gives brownish orange dyeings.

The extra hydroxyl group in the phenyl group cannot counterbalance the unfavourable effect of the meta-grouping in the benzo-nucleus.

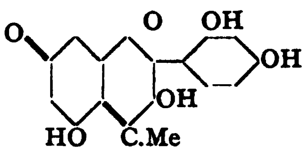
The same effect in the phenyl nucleus can be seen by comparing the last-mentioned dye with the following :—

(5) 

Violet with potassium hydroxide, mauve dyeings on alum, blue black dyeings on chrome.

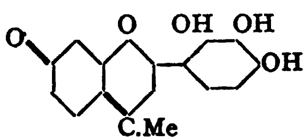
(6) 

Blue with potassium hydroxide, violet dyeings on alum and chrome.

(7) 

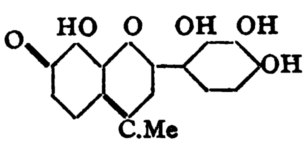
Crimson with potassium hydroxide, maroon on chrome.

The following comparisons show the tendency of three hydroxyl groups in the 1 : 2 : 3-position to produce a brown colour. Compare (1) with—

(8) 

Brownish red with potassium hydroxide, dyeings are no deeper than those given by (1).

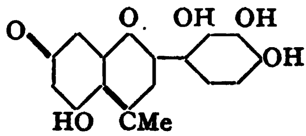
and compare (2) with—

(9) 

Violet red with potassium hydroxide, dyeing on chrome is brown similar to that given by anthragallol.

The favourable effect of the *o*-grouping in the benzo-nucleus is eclipsed by the effect of the 1 : 2 : 3-grouping in the phenyl group.

Compare (5) with—

(10)  Dark red with potassium hydroxide."

At present no explanation or mechanical analogy is forthcoming as to why the *ortho-*, *para-*, or 1.2.4 position of auxochromes should be specially favourable for the production of deep colour, whilst the *meta-*, 1.2.3 and 1.3.5 positions should be unfavourable. It was thought perhaps the ultra-violet absorption spectra of the di- and tri-hydroxybenzenes would show a similar difference, but this is not the case. (See. Figs. 25, 26 and 27, Chap. IV.)

Mention has already been made of Krüss's observations on the colour and absorption spectra of amino-indigo and amino-alizarin, from which it appears that under some circumstances additional auxochromes may lighten the colour instead of deepening it. We see a similar effect in the triphenylmethane group. Dyes of this group which have auxochromes in two only of the three benzene nuclei have deeper colours, and the band of least frequency is nearer the red end of the spectrum than in those dyes which have auxochromes in all three benzene nuclei, *e.g.* Doebner's violet has a deeper colour than *p*-rosaniline, malachite green a deeper colour than hexamethyl-*p*-rosaniline, 4 : hydroxy-malachite green—

$$OH.C_6H_4.C(C_6H_4.NMe_2) : C_6H_4 : NMe_2Cl,$$

3 : 4 : dihydroxymalachite green—

$$(OH)_2 C_6H_3. C(C_6H_4NMe_2) : C_6H_4 : NMe_2Cl,$$

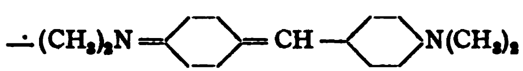
or 2 : 3 : 4 : trihydroxymalachite green—

$$(OH)_3C_6H_2. C(C_6H_4NMe_2) : C_6H_4 : NMe_2Cl ;$$

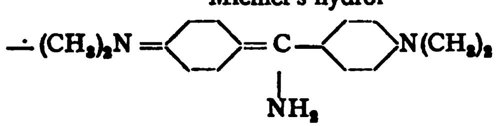
and benzaurin has a deeper colour than aurin.

Ghosh and Watson (*Chem. Soc. Trans.* 1917, *111*, 821) have offered the following explanation of this effect: "It seems possible to explain this effect by means of the theory put forward by one of us (Watson and Meek, *ibid.* 1915, *107*, 1567) as to the nature of the vibrations causing the colour of dyes. In Doebner's violet, malachite green, and benzaurin the vibration passes backwards and forwards through two of the benzene nuclei. In pararosaniline, hexamethylpararosaniline and aurin the vibratory pulse, after passing through one benzene nucleus, finds two paths open to it, as each of the remaining nuclei is now capable of vibration. We may find a mechanical analogy by comparing the transverse vibrations of a string with that of a system of three strings, each of half its length, tied together at one point and all under the same tension, so that they make equal angles with one another. Such a system will vibrate quicker than the simple string. In the same way, when all three nuclei of the triphenylmethane molecule are capable of vibrating, the period is less than when the vibration is confined to two of the nuclei."

Mention may be made here of Straus and Zeime's discussion (*Ber.* 1913, *46*, 2267) of the colours of Michler's hydrol (blue) and auramine (yellow)—

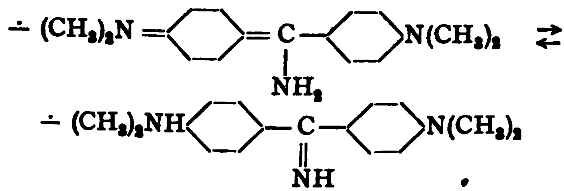


Michler's hydrol

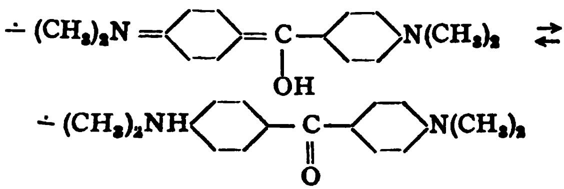


These investigators consider that the additional amino-group in auramine has so great a bathychromic effect that the blue of Michler's hydrol has been changed to yellow "of the second order." But this view seems unnecessary. In the first place the amino-group in auramine is not an auxochrome. We have no reason to regard hydroxyl, amino- or substituted amino-groups as auxochromes except when they are contained in aromatic nuclei, and this amino-

group is not attached to the benzene nuclei but to the methane carbon atom. Its effect in lightening the colour is explained by the fact that the molecule is no longer permanently quinonoid, but can now assume a non-quinonoid form, and is in fact very similar to the almost colourless Michler's ketone—



Auramine



CHAPTER VI

THEORIES ON THE NATURE OF THE VIBRATIONS CAUSING ABSORPTION BANDS AND COLOUR

BALY AND DESCH'S THEORY: BANDS DUE TO DYNAMIC ISOMERISM

These investigators studied the absorption spectra under different conditions of ethyl acetoacetate, acetylacetone, benzoylacetone, ethyl benzoylacetate, ethylacetone dicarboxylate, ethyl oxalacetate, ethyl acetylsuccinate, ethyl diacetylsuccinate, ethyl benzoylsuccinate, etc. (*Chem. Soc. Trans.* 1904, *85*, 1029 *et seq.*; 1905, *87*, 766 *et seq.*) In all these cases there is chemical evidence that the substance can exist in two tautomeric forms, the ketonic and the enolic—

$$-CH_2-CO- \quad \leftrightarrows \quad -CH=C(OH)-$$

In all cases the substances show a very definite absorption band in the presence of caustic soda or in the form of other metallic derivatives, such as the aluminium, glucinum and thorium compounds. In the presence of caustic soda the band is more pronounced the greater the proportion of alkali. Some of the substances show absorption bands in the free state and in alcoholic or aqueous solutions: *e.g.* acetylacetone, benzoylacetone, ethyl benzoylacetate and ethyl benzoyl succinate. The absorption bands of the free substance and of its metallic derivatives occur in almost the same part of the spectrum, *e.g.* acetylacetone itself has an absorption band of frequency about 3650 and its glucinum, aluminium and thorium compounds exhibit bands of frequencies 3470, 3500 and 3600 respectively; ethyl benzoylacetate has a band at 3500 and its aluminium and sodium compounds at 3500 and 3300 respectively. Baly and Desch

first reported that ethyl acetoacetate in the free state shows no absorption band (*Chem. Soc. Trans.* 1904, *85*, 1035. Fig. 3 (2)); but later examination (Stewart and Baly, *ibid.* 1906, *89*, 493) of thicker layers of solution showed that the absorption curve of an alcoholic solution contains at any rate two points of inflexion, apparently indicating incipient bands at about 3400 and 4000. In the presence of sodium hydroxide the absorption band occurs at about 3700. (The absorption curves of some of these substances have been reproduced in Figs. 18, 19, and 20.)

At the time this investigation was carried out it would probably have been most natural to assume that the absorption bands exhibited were due to one or other of the tautomeric forms. And as acetylacetone had been shown by Sir W. Perkin (*Chem. Soc. Trans.* 1892, *61*, 800), by means of magnetic rotation experiments, to contain about 70 per cent. of the di-enolic form, whilst ethyl acetoacetate was known to be almost entirely ketonic in the free state, it would have been natural to consider the absorption band as a characteristic property of the enolic form and the metallic derivatives. But Baly and Desch examined also the absorption spectrum of ethyl β-ethoxycrotonate in which the enolic form, so to speak, has been fixed by ethylation of the hydroxyl group, CH_3—C(OEt)=CH.COOEt, and found no band, whereas one would have been expected if the arrangement $\begin{array}{c} -\mathrm{C}=\mathrm{CH}- \\ | \\ \mathrm{O} \\ | \end{array}$ were the cause of it; likewise ethyl ethoxyfumarate showed no band. They came, therefore, to the conclusion that the absorption band was not due to either of the isomerides, but, rather, to the process of tautomerism by which the two forms were continually changing, the one into the other. They state that alkalies have been shown by Lapworth and others to increase the velocity of change between such isomerides, that is to say, they increase the number of molecules in the state of change. On the other hand hydrochloric acid is known to have

a restraining influence on such changes. It would follow, therefore, from Baly and Desch's theory, that alkalies should make the absorption bands of these substances more pronounced, as we have seen to be the case. [On the other hand hydrochloric acid should render the bands less conspicuous. But they state "hydrochloric acid has no action on acetylacetone."]

It is important to note to what extent Baly and Desch permitted themselves to generalise on dynamic isomerism as the cause of absorption bands. To quote their own words: "It appears, therefore, that the simple dynamic isomerism occurring in these compounds gives rise to absorption bands, and it is not too much to expect that, generally speaking, absorption bands in all spectra of this type are due to some such isomerism." Again: "Firstly, no organic substance shows an absorption band unless a possibility of tautomerism exists in the molecule. Secondly, this tautomerism need not be due to a labile atom, but may be of the same order as that occurring in those aromatic substances containing the true benzenoid structure."

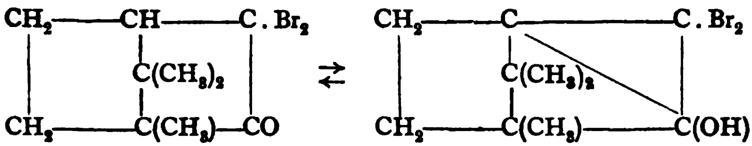
Apparently this theory has been abandoned by its authors. At any rate Desch is one of the authors of two papers on the absorption spectra of camphor derivatives (Lowry and Desch, *Chem. Soc. Trans.* 1909, *95*, 807 *et seq.*, 1340 *et seq.*; Lowry, Desch, and Southgate, *ibid.* 1910, *97*, 899 *et seq.*), in which the conclusion is formed that substances incapable of tautomerism can exhibit absorption bands.

Baly has more recently put forward a theory that absorption bands in the visible and ultra-violet are due to overtones or summation- or difference-tones derived from fundamental slower vibrations causing bands in the infra-red part of the spectrum. So that, apparently, he also has abandoned this theory of dynamic isomerism as the cause of absorption bands in the visible and ultra-violet.

The arguments brought against this theory are: (1) that some substances incapable of undergoing tautomeric change show absorption bands; (2) that some substances which

are known to be a mixture of tautomeric forms do not exhibit absorption bands.

αα-Dibromcamphor and *αα*-brommethylcamphor have been given as instances of substances which are incapable of tautomerism and yet exhibit absorption bands. To the present writer, however, it seems that tautomerism of these substances is conceivable, thus—



There is a good deal of evidence that the crystalline form of a substance corresponds to the form of the molecule, and that the form of the molecule can be ascertained by packing together the atoms contained in it (*Barlow-Pope Theory*). This would seem to indicate that the atoms in a molecule of a crystalline substance have definite fixed positions. The examination of crystals by the X-rays also apparently gives us an insight into the arrangement of atoms in the molecules of crystalline substances and indicates that they have definite fixed arrangements. This would appear to exclude the possibility of tautomerism in crystalline substances, and would exclude tautomerism as an explanation of the colour of coloured crystalline substances.

Ethyl acetoacetate is generally cited as a mixture of two tautomeric forms which exhibits no absorption band. But, as already mentioned, in a later paper Stewart and Baly showed that this substance does give indications of an absorption band (or bands). Moreover the amount of the enolic form in this substance in the free state is very small —only a few per cents.

Lowry and Desch (*loc. cit.*) studied carefully the case of nitrocamphor, a substance which exists in two tautomeric forms which can be isolated. The equilibrium between the two forms in various solvents can be studied very exactly by measuring the optical rotation, as the two forms have

different rotations. By altering the solvent it is possible to vary at will the velocity of tautomeric change, to accelerate or retard it, or to stop it altogether. Now according to the theory under discussion the prominence of the absorption band is proportional to the velocity of change between the isomerides, so that it should have been possible in this case to make the band prominent or insignificant at will. However, in spite of the wide range of velocities no great alteration was seen in the absorption curve which showed under all conditions a "step-out"; *i.e.* a point of inflexion, but no band. It was concluded that the tautomeric change did not cause a band.

It may be argued that in this case the absorption band lies beyond the range of the ordinary quartz spectroscope, which absorbs all rays beyond a certain frequency.

Since this work was published, our knowledge of the tautomerism of ethyl acetoacetate and similar substances has been considerably extended—for example, by the isolation of the tautomeric forms in pure condition (Knorr, Rothe and Averbeck, *Ber.* 1911, *44*, 1138, 2767); and it seems to the present writer that it would be well worth while to investigate this matter somewhat further, *e.g.* by examining the absorption spectra of the pure isomerides of acetylacetone, benzoylacetone, ethyl benzoylacetate and ethyl benzoylsuccinate. Obviously if the theory is true the pure isomerides should show no absorption bands. Again, the dialkyl derivatives of these substances, as, *e.g.* ethyl diethylbenzoylacetate, $CH_3.COC(C_2H_5)_2COOC_2H_5$, should show no absorption bands, as the possibility of tautomerism has been removed.

STEWART AND BALY'S THEORY OF ISORROPESIS AS A CAUSE OF SELECTIVE ABSORPTION. (Stewart and Baly, *loc. cit.*)

Shortly after the publication of the theory above mentioned it was recognised that some substances exhibited absorption bands, although there was no evidence that they could exist in tautomeric forms, *e.g.* acetone and other simple fatty ketones such as methyl ethyl ketone, methyl

propyl ketone, methyl *iso*propyl ketone, etc. It is, however, easy to imagine a tautomeric change in these substances, for example—

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \quad \leftrightarrows \quad CH_3-\underset{\underset{OH}{|}}{C}=CH_2$$

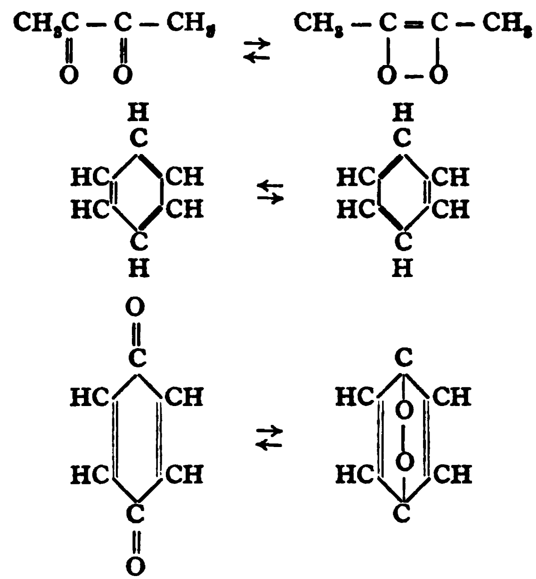
And, in fact, it is now generally considered that such processes as bromination are due to the addition of bromine at the double bond of the enolic form with the subsequent removal of water—

$$CH_3-\underset{\underset{O}{\|}}{C}-CH_3 \rightarrow CH_3-\underset{\underset{OH}{|}}{C}=CH_2 \rightarrow CH_3-\underset{\underset{OH}{|}}{CBr}-CH_2Br$$
$$\rightarrow CH_3-CO-CH_2Br$$

so that at the present time chemists would find no difficulty in admitting the possibility of tautomerism in acetone, etc.

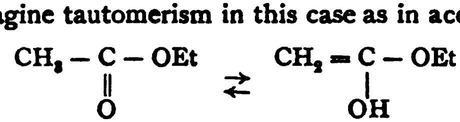
But it was also recognised that other substances exhibited absorption bands, for which there seemed no possibility of tautomerism in the ordinary sense, *i.e.* tautomerism involving the migration of a hydrogen atom, *e.g.* ethyl pyruvate, $CH_3CO.COOEt$, diacetyl, $CH_3CO.COCH_3$, benzene and benzoquinone.

Stewart and Baly observed that there seemed to be some sort of connection between chemical reactivity and selective absorption, *e.g.* those ketones which reacted most readily with sodium bisulphite showed the strongest absorption bands. Proceeding on the idea that nascent substances are frequently more reactive than the same substances in the ordinary condition, they were able to imagine molecular rearrangements of the above-mentioned substances, which would have the effect of presenting the ketonic groups in the nascent condition. But without introducing this idea of a connection between chemical reactivity and selective absorption we may simply notice that Stewart and Baly pointed out that for all these substances it was possible to imagine a vibration between two forms in which the valencies were differently arranged; for example—



Such molecular rearrangement, not involving the migration of a hydrogen atom, was termed "Isorropesis" by these investigators, and they advanced the theory that this kind of dynamic isomerism was also capable of producing selective absorption.

In criticism of this theory it may be noted that acetic acid and ethyl acetate show no signs of selective absorption (Hartley and Huntington, *Phil. Trans. I.* (1879) 257; Schönn, *Wied Ann. 6* (new series) 1879, 267), whilst it is as easy to imagine tautomerism in this case as in acetone, viz.—



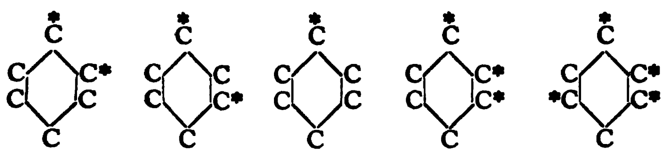
Stewart and Baly would probably have argued that this tautomerism does not occur, since ethyl acetate does not react with sodium bisulphite. But at the present time chemists postulate such a change in order to explain the bromination of this ester, in the same way as has been explained in the case of acetone.

Pursuing this idea of dynamic isomerism as a cause of

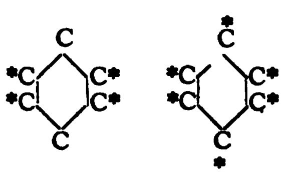
absorption bands, Baly and Collie (*Chem. Soc. Trans.* 1905, *87*, 1335) claimed that they could account for the seven bands of benzene. As their reasoning is not clear to the present writer their own words are quoted: "In the light of the work on the aliphatic tautomeric compounds it is only possible for us to establish all the possible phases of linking change and to attribute a band to each. Now, in considering all this possible making and breaking of links, we are justified in assuming that an even number of carbon atoms is concerned in each individual process. The process in the aliphatic compounds, on being reduced to its simplest terms, consists of at least two separate items, namely, the make and break between the two carbon atoms and that between the carbon and the oxygen atoms, thus—

the stars being attached to those atoms which are undergoing the linking change.

"In applying this to benzene we may, therefore, differentiate between the transition phases in which any pair of the carbon atoms, or any four, or all of the six, are concerned. The various transition phases may, therefore, be represented as follows—



(1) (2) (3) (4) (5)



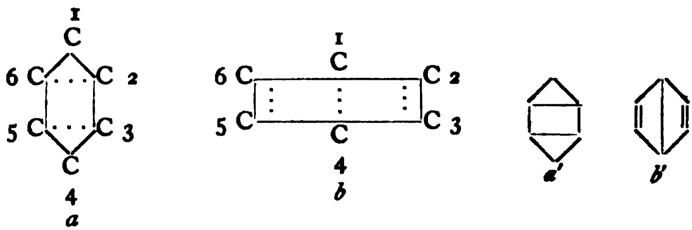
(6) (7)

the stars again being attached to those carbon atoms which are concerned in the process.

"These seven forms represent all the possible conditions of making and breaking the linkings which can occur, and at the same time they are so different in character as to justify the view that each of them is the origin of a separate absorption band."

The subject was further explained by Baly, Edwards, and Stewart (*ibid.* 1906, *89*, 524). Again the explanation is not clear to the present writer but is quoted—

"Now in order to bring the seven phases into existence it is necessary to assume the displacement of the carbon atoms of the ring, and we can do this in the simplest way possible, that is to say, by the ordinary vibration as is accepted by any elastic ring. Thus we may say that the benzene ring is pulsating between the two displaced forms *a* and *b*.



"Each carbon has residual affinity, and consequently in the condition represented in *a*, when the atoms 2 and 6 and the atoms 3 and 5 are brought close together, these residual affinities will produce linkings as shown by the dotted lines. The atoms 1 and 4, however, are far removed from one another and from the other atoms, and are, therefore, unsaturated. On the other hand, when the ring has passed into the other phase, *b*, then the three atoms 2, 1 and 6 come very close to the three atoms 3, 4 and 5 respectively, and linking may be considered to be formed between these pairs of atoms. The linkings existing in phases *a* and *b* are shown for greater convenience on the ordinary hexagons in *a′* and *b′*. As the ring is pulsating between the forms *a* and *b*, many of the seven phases of linking change described above will be

obtained. For example, let us consider the ring to have reached the form *b*; as it starts opening, the first break will occur between the atoms 1 and 4, followed by the breaking of the two ortho-linkings 2 : 3 and 5 : 6. When the ring passes through the half-way stage, that is, the circular form, then we shall have the centric formula, with the result that phase No. 7 is produced. We can in this way account for phases 1, 2, 3, 6 and 7; Nos. 4 and 5 can readily be understood if the motions described above are slightly interfered with by collisions between adjacent molecules."

Theory that the Vibrations causing the Absorption Bands of Dyes and Coloured Substances are those of the Parent Substances modified and rendered less rapid by the Introduction of Chromophores and Auxochromes

This theory has been held or used as a working hypothesis by most workers on the relation between colour and constitution. It was, perhaps, first advanced by Hartley, when he published the absorption curves of some triphenylmethane and azo-dyes (*Chem. Soc. Trans.* 1887, *51*, 154 *et seq.*). He said: "On carefully comparing the curves of the rosaniline series of dyes, triphenylmethane and benzene, it is seen that they are modifications of the benzene curve; but the closeness of the relationship of the triphenylmethane curve to the dyes is much greater than that of the benzene series, and the curves of the three dyes are modified in such a manner that they follow each other closely. The modification is such that the molecules of greatest mass transmit least light; and the light is composed of rays vibrating with least rapidity, thus indicating a greater amplitude and less rapidity of vibration of the molecule. The same remark applies to the diazo-colours. They all present curves which are modifications of the azo-benzene curve."

We have already described how Baly regarded the absorption bands of benzene as due to a complex series of "isorropeses," and claimed to deduce from his "isorropesis"

theory that there would be seven—and only seven—benzene absorption bands. He then went on to study the absorption spectra of some simple mono- and di-derivatives of benzene. Some of these have several narrow bands in almost exactly the same places as benzene bands; in others there are only one or two of these narrow bands left; and, finally, in nitrobenzene they all vanish and the absorption spectrum consists of one broad band (or, to be more exact, the absorption curve is inflected indicating such a band), covering the part of the spectrum occupied by the benzene bands and extending beyond it. He came to the conclusion that, in most cases, the absorption bands were due to the vibrations of the benzene ring more or less modified by the presence of the attached groups: the modification being greatest in the case of nitrobenzene, where, he supposed, the making and breaking of the linkings between the carbon atoms had ceased. [But he regarded the absorption bands of the mono- and di-hydric phenols and the aminophenols as due to another cause, viz. ordinary tautomerism.] Baly and Tuck (*Chem. Soc. Trans.* 1906, *89*, 982) came to the conclusion that the absorption of azobenzene was due to modified vibrations of the benzene nuclei. Tuck (*ibid.* 1907, *91*, 449 *et seq.*; 1909, *95*, 1809 *et seq.*) then examined the absorption spectra of some simple azo-dyes, and considered that their vibrations were modifications of the azobenzene vibration in the same way as those of the simple derivatives of benzene were modifications of the benzene vibrations—"the colour band of azobenzene was modified by substituting groups in a similar manner to the effect produced by the same groups on the absorption spectrum of benzene." Later on Tuck was impressed by the fact that the absorption curves of *p*-aminoazobenzene and the sodium salt of *p*-hydroxyazobenzene were practically identical, that those of aniline and sodium phenoxide were also practically identical and that the addition of sodium ethoxide shifted the absorption bands of phenol and *p*-hydroxyazobenzene forward towards the red end of the spectrum in the same way. "This," he says, "renders it probable that the bands of aminoazobenzene and the sodium salt of benzeneazophenol are

merely those of aniline and sodium phenoxide respectively shifted into the visible region by conjugation with the unsaturated group . N : N . C_6H_5."

Meyer and Fischer (*Ber.* 1913, *46*, 70 *et seq.*), after an examination of the absorption curves of some triphenylmethane dyes, came to the conclusion: "Vielmehr bestätigt sich die Hartleysche Theorie, nach welcher der eigentliche Farbträger stets der Benzolkern ist. Die Chromophore verschieben die absorption aus dem kurzwelligen in den langwelligen Teil des Spektrums und die Auxochromen Gruppen verstärken und unterstützen—entsprechend ihrem Namen—diese Wirkung der Chromophore."

This theory has been criticised by Watson and Meek (*Chem. Soc. Trans.* 1915, *107*, 1573–4) as follows—

"Until recently, the general view as to the relation between constitution and absorption spectra seemed to be that the absorption bands of dyes were those of the parent substances, moved towards the red end of the spectrum by the introduction of chromophores into the molecule, and strengthened, and probably also moved towards the red, by auxochromes (Hartley, *Trans.* 1887, *51*, 154; Tuck, *Trans.* 1907, *91*, 449; 1909, *95*, 1809; Meyer and Fischer, *Ber.* 1913, *46*, 82). It was left rather indefinite as to what should be considered the parent substance of any particular dye; for example, in the case of the triphenylmethane dyes, either fuchsone or triphenylmethane or benzene might equally well be regarded as the parent substance. Tuck, in the course of his investigation on hydroxyazo dyes, at one time recognised the band of hydroxyazobenzene as that of phenol moved towards the red by the influence of the benzeneazo-group, and at another time regarded it as that of azobenzene shifted by the hydroxyl group. It scarcely seems possible for it to be both. Take, again, the anthraquinone dyes. If benzene is regarded as the parent substance they should all have seven bands, or if anthraquinone is taken as the parent they would all be expected to have the bands of that substance. Anthraquinone itself has two or three bands according to the solvent in which it is examined (Baly and Stewart T., 1906, *89*, 511;

Meyer and Fischer, *Ber.* 1913, *46*, 89), and there are hydroxy-derivatives which in some circumstances show only one, others which show two, three and four bands (Meyer and Fischer, *loc. cit.* pp. 74 *et seq.*), so that it requires the liveliest imagination to recognise the bands of any derivative as those of the parent substance. Even in cases in which there is a superficial resemblance between the absorption curves of two substances, for example, fuchsonimonium chloride and Doebner's violet (Meyer and Fischer *loc. cit.*), the resemblance is only superficial. The different bands are not shifted to the same extent nor do they retain the same relative intensity. Analysis of the curves given by Meyer and Fischer shows the following—

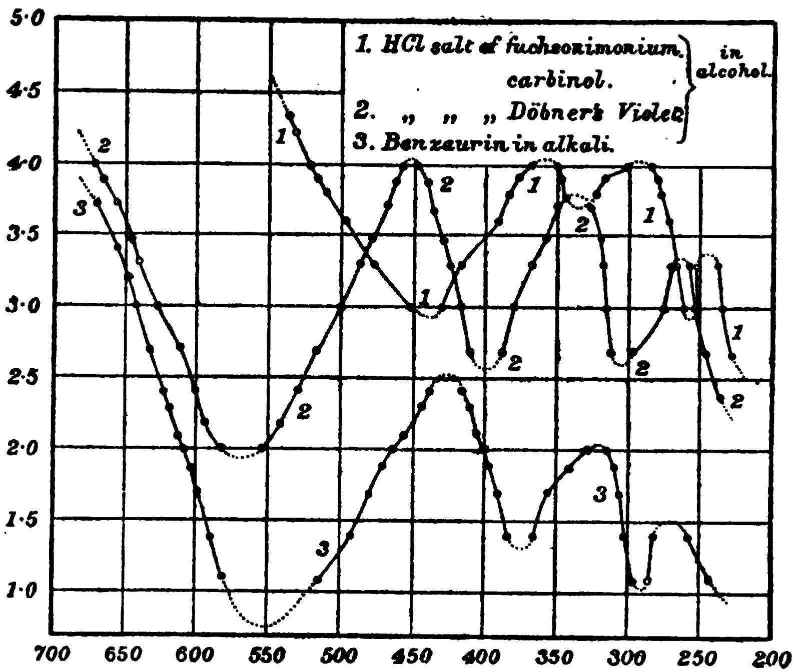


FIG. 59.

(Reproduced from Meyer and Fischer's paper, *Ber.*, 1913, 46, p. 74, Fig. 2.)

	Fuchsonimonium chloride (λ)	Doebner's violet (λ').	λ' − λ	λ'/λ.
Maxima of absorption bands	(1) 430 (2) 330 (3) 260	565 400 305	135 70 45	1·311 1·212 1·173

	Fuchsonimonium chloride.	Doebner's violet.	Relative intensity of bands in two substances.
Concentrations at which bands first appear	(1) 700 (2) 5000 (3) 800	80 400 450	8·7 12·5 1·5

It is, therefore, difficult to see how the bands of one substance can be identified with those of the other."

WATSON AND MEEK'S THEORY

In the chapter on the relation between constitution and depth of colour, an account was given of some work leading to the conclusion that, *cæteris paribus*, the depth of colour or the period of the principal absorption band is proportional to the length of conjugate chain reversed during tautomeric change. This naturally led to the theory that this reversal of the conjugate chain is the vibration causing the principal absorption band and the characteristic colour (*Chem. Soc. Trans.* 1915, *107*, 1567 *et seq.*)—

"The change from one quinonoid form to another involves the changing of places of double and single bonds all along the chain of conjugate double and single bonds. A pulse, something like that which is seen when a goods train is shunting, passes in one direction along the conjugate chain as the substance changes from one form to another, and back again as the reverse change takes place. It is suggested that this pulse is the vibration which causes the colour of dyes. It is a somewhat peculiar kind of vibration. When the substance is in the ionised condition, as is always the case under

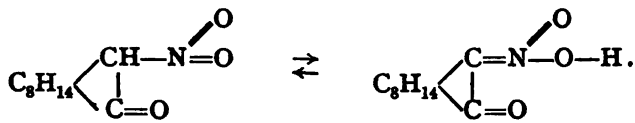
the conditions which develop the deepest and most intense colour of dyes—for example, in aqueous dilute acid solution of basic dyes or aqueous dilute alkaline solution of acid dyes—there is no vibration of the atoms of the molecule, but only a rhythmic rearrangement of the strains in the molecule. Even when the substance is not ionised, the only atom which must necessarily move is the hydrogen atom concerned in the tautomerism. (It seems quite possible that this rhythmic rearrangement of strains might be going on in a molecule without the tautomerism ever actually being achieved, somewhat as the engine of a motor-car may be working but unable to set the car in motion.) When the mass vibrating is small, we have the conditions under which forced vibrations can be set up. Now one of the most striking features of the absorption bands of dyes is their breadth and indefiniteness, suggesting forced vibrations. One of us is pointing out elsewhere that the absorption bands of dyes are frequently asymmetrical, and that this would be expected in the case of forced vibrations.

"In a shunting goods train, the time taken for a pulse to pass down the train is proportional to the number of wagons, provided the wagons are all of the same kind and equally loaded. From analogy we predicted that in very similar molecules the period of the principal vibration causing colour would be proportional to the length of the conjugate chain." The experiments confirming this prediction have already been described in Chapter V.

It will be noted that this theory is an extension of Baly's theory of isomeric change as the cause of selective absorption. We have already examined the arguments brought forward against it. It may be noted that by this theory a rough calculation can be made as to the position which we should expect the absorption band of ethyl acetoacetate to occupy. When a conjugate chain containing five double bonds is reversed, as in Michler's hydrol, the maximum of the absorption band has a wave-length of about 6000. In the tautomerism of ethyl acetoacetate there is reversal of a conjugate chain containing two double bonds, so we should

expect the absorption band to have a wave-length of approximately $\frac{2}{5} \times 6000 = 2400$. The absorption band lies about λ 2400 — 2500.

Lowry and Desch have shown that the dynamic isomerism of nitrocamphor in acid solution does not produce any observable absorption band.



But in this case the tautomerism only involves a chain of one double and one single bond, and, according to this theory, the oscillation from one form to the other would be so rapid (roughly λ 1200) that the corresponding absorption band would lie quite outside the range of the quartz spectroscope.

But the theory will not account for the blue colour of the tertiary nitroso-fatty compounds which contain no reversible conjugate chain.

THEORY THAT ABSORPTION BANDS ARE DUE TO THE VIBRATIONS OF ELECTRONS, *i. e.* NEGATIVELY CHARGED PARTICLES OF ONLY ABOUT $\frac{1}{1000}$TH OF THE MASS OF THE HYDROGEN ATOM

An account of this theory will be found in Campbell's "Modern Electrical Theory" (*Camb. Univ. Press*, 1913). Apparently the first calculation as to the number and mass of the electrically charged particles causing refraction and absorption was made by Drude. Other calculations are given in the following papers:—Erfle, *Ann. d. Phys.* *24*, 672, 1907; Koenisberger and Kilchling, *ibid.* *28*, 889, 1909; *32*, 843, 1910.

It is difficult to find a non-mathematical account of this theory. But its claims are put forward sufficiently clearly by Campbell (*loc. cit.* pp. 315 and 316): "To the first class belong the lines which give to many artificial dyes their intense colour. . . . In the first class it is found . . . the absorption

band represents the natural frequency of one electron in the molecule." "It must be remembered—for the point is usually ignored by chemists—that in all cases which have been investigated the intense absorption bands which cause the colour of dyes represent the vibrations of electrons, and not of entire atoms or groups of atoms."

The electro-magnetic theory of light is generally accepted. According to this theory, light waves are waves of electro-magnetic disturbance. The refraction and absorption of light can only be explained on any wave-theory as due to the presence of vibrating particles in the refracting and absorbing medium, and the electro-magnetic wave-theory requires these particles to be electrically charged.

If we know for any medium the values of the refractive index for light of different wave-lengths—and this can be determined experimentally—we can calculate the number per unit volume of the electrically charged particles causing the refraction, also their mass and their period of vibration; to be more correct we can calculate their period of vibration and the value of the expression $\frac{pe}{m}$, where p is the number of particles per molecule, e the electrical charge carried by an atom, and m the mass of the particles.

By making certain assumptions we can deduce from the electro-magnetic theory that—

$$n^2 = B_o + \Sigma \frac{B_n}{\lambda^2 - \lambda_n{}^2}$$

where n is the refractive index for light of wave-length λ and λ_n is the wave-length corresponding to the frequency of the vibrating particles causing the refraction, and—

$$B_n = \frac{N_n e^2 \lambda_n{}^4}{\pi m_o c^2}$$

where N_n is the number per unit volume of the vibrating particles causing the refraction—

e is the charge carried by an atom;

m_o is the mass of the vibrating particles;

c is the velocity of light.

B_n can be calculated when the refractive index for light of different wave-lengths has been determined.

Now—

$$N_n = pN'$$

where p is the number of particles per molecule, and N' is the number of molecules per unit volume.

The number of molecules per unit volume can be determined from the density and molecular weight, the mass of a hydrogen atom being known—

$$N' = \frac{d}{Wm_h}$$

where d = density of the substance;

W = molecular weight;

m_h = mass of a hydrogen atom $= 2\cdot894 \times 10^{-14}e$;

where e is the electrical charge carried by a hydrogen atom;

$\therefore$ we have—

$$\frac{pe}{m} = \frac{B_n}{\lambda_n^4} \times \frac{W}{d} \times \frac{\pi c^2}{2\cdot894 \times 10^{14}}$$

From this expression we can calculate the number, mass, etc., of the electrified particles causing refraction.

If we take into account the absorption as well as the refraction of light by a medium, the following expression can also be deduced from the electro-magnetic theory (again, by making certain assumptions and approximations)—

$$n^2K = \frac{N_e e^2 k\nu}{4\pi^2 m_e^2(\nu_e^2 - \nu^2) + k^2\nu^2}$$

where—

n = refractive index for light of frequency ν;

K = coefficient of absorption for light of refractive index n

k = a constant representing the frictional force acting on the vibrating particles.

Other terms as before.

So that we can calculate $\frac{pe}{m}$ also from the refractive index of light in the region of absorption, the coefficient of absorption, and the other quantities as before.

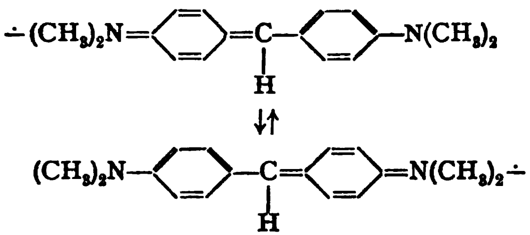
According to Campbell (*loc. cit.*), it has been found that

for the absorption bands of some artificial dyes $\frac{pe}{m}$ has a value agreeing with the assumption that the absorption band is due to only one vibrating particle per molecule, this particle having the usual mass and electric charge of an electron. It is on the strength of this result that Campbell says: "It must be remembered—for the point is usually ignored by chemists—that in all cases which have been investigated the intense absorption bands which cause the colour of dyes represent the vibrations of electrons, and not of entire atoms or groups of atoms."

It would be of considerable interest to the chemist, or to any one studying the relation between colour and constitution, if it were definitely proved that each absorption band is due to one, and only one, vibrating electron. But as a matter of fact the above-mentioned conclusion was arrived at from the study of a very small number of dyes, and Meek (*Chem. Soc. Trans.* 1917, *111*, 984) has recently shown that for some absorption bands of the polyhydroxyanthraquinones the value $\frac{pe}{m}$ is several times as great as for others.

Substance.	Relative values of m/pe for elementary bands.		
	Band No. 1.	Band No. 2.	Band No. 3.
Alizarin . . .	7	1	—
Quinizarin . . .	1	1	3
Purpurin . . .	2	1	—
Anthragallol . .	4	2	1

It may also be pointed out that this conclusion, viz. that the absorption bands of some dyes are due to the vibrations of a limited number of electrons, does not prevent the acceptance of a theory postulating tautomeric change as the cause of absorption bands. Take, for example, the case of Michler's hydrol, which exhibits a deep blue colour in dilute acid solution. In such a solution the hydrochloride will no doubt be completely ionised. According to Watson and Meek's theory, the colour is due to an oscillatory interchange of double and single bonds along the conjugate chain—



If we suppose that a bond between two atoms indicates that an electron from one of the atoms has passed into the other, then this breaking of five double bonds and formation of five new double bonds involves the movement of five electrons. As the substance is ionised, it is unnecessary to assume the movement of any atom.

Most dyes exhibit their deepest and strongest colour when ionised, *e.g.* acid dyes in dilute alkaline solution and basic dyes in dilute acid solution, and when the substance is ionised tautomerism does not involve the oscillation of any atom backwards and forwards from one part of the molecule to another. It is equally obvious that Baly's theory of isorropesis does not involve the vibration of atoms.

In the same paragraph in which Campbell states that it has been found the absorption bands of dyes are due to one vibrating electron he says: "It is found that absorption bands (of solids and liquids at least) can be divided into two classes; first, narrow absorption lines in which the absorption is very intense and accompanied by metallic reflection of the light 'absorbed'; second, much broader absorption bands in which the absorption is much less intense and unaccompanied by any special reflection. To the first class belong the lines which give to many artificial dyes their intense colour; to the second the bands to which the colour of such substances as copper sulphate is due. In the first class it is found that the value of p for the molecule is about 1; the absorption band represents the natural frequency of one electron in the molecule. In the second class pe/m turns out to be of the order of 10^{15}, instead of 10^{18}, so that if we regard the vibrating system as an electron, there can only be one electron

concerned in about 1000 molecules. On the other hand, if we regard the vibrating system as an atom, we should often have to suppose that the atom carried a charge of more than $100e$."

The present writer is unaware to what extent the absorption bands of dyes and coloured organic substances have been examined for metallic reflexion of the light absorbed. But certainly there are no dyes which give absorption bands fine enough to be called lines, and many of the bands are very broad. There would seem to be no difficulty about supposing that such broad absorption bands may be due to the oscillation of hydrogen atoms, which are the atoms usually supposed to oscillate in tautomeric change, and which have a mass about 2000 times that of the electrons. With $p = 1$, and e having the usual value, $\frac{pe}{m}$ would then have a value of the order of 10^{15}.

But in the opinion of the present writer the weakest part about this development of the electro-magnetic theory is that it does not account in any way for the great breadth and indefiniteness of absorption bands in general. We are acquainted with sharp line spectra, as, *e.g.* flame and arc spectra, and also we know some substances which exhibit a large number of very narrow absorption bands when their vapours are examined under reduced pressure, *e.g.* benzene and benzoquinone. Presumably these lines and very narrow bands are due to electronic vibrations. And if the ordinary broad absorption bands are also due to the vibration of a strictly limited number of electrons, in what way do these electrons differ from those which cause the lines or narrow bands? One of the equations given involves a constant k, which represents the frictional force acting on the vibrating particles. But why are the vibrating particles causing the broad absorption bands of dyes opposed by frictional forces of such a very different magnitude from those acting on other vibrating electrons? There is good reason to believe that the ordinary absorption bands of organic substances are really composed of a large number of fine bands which are not

resolved under ordinary conditions. This seems to be quite incompatible with the view that these ordinary bands are due to the vibration of one or a strictly limited number of electrons.

Baly's Theory, according to which the Absorption Bands in the Visible and Ultra-violet Parts of the Spectrum can be calculated from those in the Infra-red

By an application of the "quantum" theory (*Phil. Mag.* 1914, *27*, 632 *et seq.*) Baly came to the conclusion that the frequencies of the absorption bands of a substance might be simple integral multiples of a fundamental frequency. Thus if *n* were the fundamental frequency, the substance might exhibit absorption bands corresponding to frequencies *n*, 2*n*, 3*n*, 4*n*, 5*n*, etc.

He showed that in a few cases where a substance exhibited three bands (absorption or fluorescence bands) there was the same difference between the frequencies of the first and second as between those of the second and third.

	First Absorption Band.	Second Absorption Band.	Fluorescence Band.	Differences. I.	Differences. II.
o-Aminocinnamic Acid	3600	2800	2000	800	800
β-Naphthylamine	3600	3000	2400	600	600
Benzaldehyde (in strong H_2SO_4)	3400	2174	—	2 x 613	
Benzaldehyde (in alcohol)	4070	3470	—	600	

He regards the benzaldehyde band with frequency of 3400 in strong sulphuric acid as being the same band as that with frequency 3470 in alcohol, the difference of frequency being due to the solvents.

In the case of benzene and *p*-xylene the frequencies of the centres of the groups of absorption, fluorescence, phosphorescence and cathodo-luminescence bands can be represented as integral multiples of the frequency of an infra-red band (*Phil. Mag.* 1915, *29*, 223 *et seq.*).

Benzene

Infra-red . . .	405 (Coblentz 2·49μ)
Phosphorescence . .	$6 \times 403·3$
Fluorescence . . .	9×405 *
Absorption . . .	10×405

p-Xylene

Infra-red . . .	—
Cathodo-luminescence .	8×257
Phosphorescence . .	10×256
Fluorescence . . .	14×258 *
Absorption . . .	15×258

* 14 and 13 respectively are added to the frequencies of the centres of the fluorescence bands. This is considered justifiable, because the fluorescence bands were observed in alcoholic solution.

Bjerrum (*Nernst Festschrift*, 1912, p. 90) had pointed out that if the atoms in a molecule are vibrating with a characteristic frequency producing an absorption line or band in the infra-red, we ought to observe additional bands on each side of this due to the compounding of the rotation of the molecule with the characteristic vibration. If ν is the characteristic frequency and ν_r the frequency of rotation of the molecule we might expect bands of frequencies $\nu + \nu_r$ and $\nu - \nu_r$. And according to the quantum theory the rotational frequencies must have well-defined values given by the formula—

$$\frac{hn}{2\pi^2 I}$$

where I is the moment of inertia,
h a constant,
n a whole number.

If we represent these successive values as ν_r, $2\nu_r$, $3\nu_r$, etc., then we might expect bands of frequencies, $\nu + \nu_r$, $\nu + 2\nu_r$, $\nu + 3\nu_r$, etc., $\nu - \nu_r$, $\nu - 2\nu_r$, $\nu - 3\nu_r$, etc.

Fräulein von Bahr found evidence of such a symmetrical arrangement about the absorption band of water-vapour at 6·26μ (*Phil. Mag.* 1914, *28*, 71). And Eucken (*Deutsch Phys. Ges. Verh.* XV. p. 1159 (1913), found still better agreement on the assumption of the water-molecule possessing two degrees of freedom.

Baly thought that this theory would also explain the symmetrical groups of absorption bands exhibited by benzene and other substances, such as toluene, xylene and naphthalene, in the ultra-violet, and the similar groups of fluorescence bands in the visible part of the spectrum. If ν, ν_1, ν_2, ν_3, ν_4, etc., are the frequencies of infra-red bands he suggested that there should be absorption and fluoresence bands of frequencies $n\nu \pm \nu_1$, $n\nu \pm \nu_2$, $n\nu \pm \nu_3$, etc. He found that the observed values agreed with this assumption.

In the case of absorption in the ultra-violet he studied, not the absorption bands of the substances in the liquid form or in solution or in the state of vapour under ordinary pressure, but the groups of very fine absorption bands (or lines) exhibited by these substances in the form of vapour under reduced pressure (*see* Chapter IV). These fine absorption bands, or lines, were first observed by Pauer (*Wied. Ann.* 1897, *61*, 363–379), and those of benzene were carefully measured by Hartley (*Phil. Trans.* 1908, A. 208, 520), who came to the conclusion that the ordinary broad bands were produced by the fusion of these finer bands. To quote Hartley's own words : "A solution band is thus seen to be the aggregate effect of the absorption of rays caused by a group of vapour bands, which is modified by the greater density and consequently greater dispersion of the liquid in which the substance is dissolved, and it is shifted towards the red in accordance with Kundt's rule. The slightly different positions of the four vapour spectra, their similarity in constitution and the manner in which they overlap, afford an explanation of the reason for the spectrum of benzene being composed of six principal groups of vapour bands and six corresponding solution bands."

But, apparently, the groups of absorption lines are somewhat more symmetrically arranged than the ordinary absorption bands. Thus in the case of benzene Hartley found ten groups, each with a well-marked head. Baly saw that the arrangement of these groups about the centre could be calculated from the frequencies of observed infra-red bands in the manner above indicated. In the following table are given the wave-lengths of the heads of these ten bands as

recorded by Hartley. In the second column the corresponding frequencies are given; in the third column the frequency differences between each line and the central line; and in the fourth the means between the two values where such exist. The values of $1/\nu_x$ or the wave-lengths of the infra-red bands are given in the fifth column, whilst in the last column are to be found the wave-lengths of the absorption bands as measured by Coblentz (*Publications of the Carnegie Institution, Washington*, No. 35 (1905).

λ in Ångströms.	$1/\lambda$	ν_x	Mean ν_x	Infra-red Bands.	
				Calculated.	Observed.
2670	3745	310	—	3·23μ	3·25μ
2630	3802	253	249	4·08	—
2590	3861	194	—	5·15	—
2523	3963	92	92·5	10·81	10·78
2466	4055	0	—	—	—
2411	4148	93	92·5	10·81	10·78
2360	4237	182	—	5·50	5·41
2335	4282	227	—	4·40	4·40
2326	4299	244	249	4·08	—
2279	4388	333	—	3·00	—

The fluorescence bands of benzene in alcoholic solution (Dickson, *Zeit. wiss. Phot. X.* p. 166, 1912) could be calculated from the infra-red bands in the same way.

λ in Angströms.	$1/\lambda$	ν_x	Infra-red Bands.	
			Calculated.	Observed.
2910	3436	195(194)	5·15	—
2827	3537	94(92)	10·81	10·78
2754	3631	0	—	—
2679	3733	102(101·5)	9·85	9·75
2635	3795	164(160)	6·23	6·20
2599	3848	217(208)	4·80	4·90

Baly now found that he could calculate not only the positions of the groups of lines, but even the positions of the fine lines themselves, by the application of this same principle. Coblentz had observed sixteen infra-red absorption bands of benzene between the limits 3·0 and 15μ: Baly found that each

one of these (except that at 3·23μ) gave a pair of ultra-violet lines. In this way the positions of 29 ultra-violet absorption lines were calculated.

λ in Ångströms.	$^1/_\lambda$	ν_x	Mean ν_x.	Infra-red Bands.	
				Calculated.	Observed.
2670	3745	310	—	3·23μ	3·25μ
2612	3828	227	228	4·38	4·40
2600	3847	208	208	4·80	4·90
2582	3873	182	182	5·50	5·41
2567	3895	160	160	6·23	6·20
2560	3907	148	148	6·75	6·75
2553	3917	138	138	7·25	7·22
2546	3928	127	127	7·85	7·80
2538	3940	115	115	8·67	8·67
2529	3954	101	101·5	9·85	9·78
2527	3958	97	97	10·30	10·30
2523	3963	92	92·5	10·81	10·78
2519	3970	85	85	11·80	11·80
2516	3974	81	81	12·30	12·45
2514	3978	77	77	12·95	12·95
2466	4055	0	—	—	—
2420	4132	77	77	12·95	12·95
2417	4136	81	81	12·30	12·45
2416	4140	85	85	11·80	11·80
2411	4148	93	92·5	10·81	10·78
2409	4152	97	97	10·30	10·30
2406	4157	102	101·5	9·85	9·78
2398	4170	115	115	8·67	8·67
2391	4182	127	127	7·85	7·80
2385	4193	138	138	7·25	7·22
2379	4203	148	148	6·75	6·75
2373	4215	160	160	6·23	6·20
2360	4237	182	182	5·50	5·41
2346	4263	208	208	4·80	4·90
2334	4284	229	228	4·38	4·40

But Hartley had recorded at least 300 ultra-violet absorption lines for benzene. It was interesting to see whether a further extension of the theory, which had been so successful in accounting for 31 of these lines, could be made to account for all the lines recorded (Baly, *Phil. Mag.*, 1915, *30*, 510, *et seq.*). It has already been mentioned that the arrangement of infra-red maxima of absorption about the band at 6·26μ in the case of water-vapour was in accordance with Bjerrum's theory, and Baly tried to find a similar connection between the observed infra-red bands of benzene. He came to the conclusion that all the infra-red bands could be calculated

from four numbers, which he terms basis constants. These numbers are 3·7, 4·0, 7·6, and 10·125, and the frequencies of the infra-red bands are either integral multiples of these constants or the products of two of these constants. It seems to the present writer that the relationship detected by Baly is not exactly in accordance with Bjerrum's theory; also that the detection of the basis constants required a good deal of imagination. For this reason the original paper is quoted to show how these basis constants were arrived at:—

"Now Eucken showed that the infra-red absorption bands of water-vapour of longer wave-length than about 10μ can be expressed by the Bjerrum formula; that is to say, their frequencies form consecutive multiples of two constants (he having assumed two degrees of freedom) which, if wave-length reciprocals be used, are 5·78 and 2·5 respectively. Eucken, however, entirely failed to explain the very remarkable variations in the relative intensities of the infra-red absorption bands of water. He only extended his second series to 10·0μ and offered no explanation of the extraordinary intensity of the great absorption bands of 6·0μ, 3μ, 2μ and 1·5μ. The whole essence of Bjerrum's theory is that the frequencies of the centres of the infra-red bands are consecutive multiples of a fundamental constant or basis." [It seems to the present writer that at this stage Baly drops the constant representing the natural frequency of the atoms in the molecule and considers only the term due to the rotational frequency of the molecule.] "His theory in no way accounts for the fact that certain select multiples of the constants give rise to absorption bands which are far more intense than the neighbouring multiples on each side. On the other hand, if there are two constants or bases, then there must exist a convergence-frequency of the two, as it were, which is the least common multiple of the two bases. It is to be expected that such a frequency would necessarily be especially active since it is keyed with both series. I suggest, therefore, that this is the reason why an infra-red absorption band is especially pronounced in intensity, namely, that its frequency is either an even multiple of the two bases which are active, or that it is

the least common multiple of the two bases. If this principle be accepted, it seems entirely to solve the difficulty connected with the intensity of the absorption bands, and makes the calculation of the values of the bases a simple matter."

"Benzene may be taken as the first example, and in the case of this substance there are twenty absorption bands recorded by Coblentz between the limits 1μ and 13μ. These vary very much between themselves in intensity, and the most pronounced bands are at 9·78, 6·75, 3·25, 2·48, 2·18 and $1{\cdot}68\mu$. Now if the wave-numbers [reciprocals of the wave-lengths—must be multiplied by 3×10^8 to convert into true oscillation frequencies] of all the infra-red benzene bands be considered, it will at once be seen that they are nearly all multiples of 4, and indeed it appeared at first sight as if they all could be expressed with very fair accuracy as multiples of 4. This, however, gives no explanation of the remarkable intensity differences in the bands, and, further, all the consecutive multiples of 4 do not appear as bands, even between 10μ and 13μ, where perhaps they might be expected to evidence themselves. The two most characteristic and outstanding bands are those at $3{\cdot}26\mu$ and $6{\cdot}75\mu$, and the wave-numbers of these are almost exactly 308 and 148, and on the least common multiple principle these may be looked upon as the least common multiples of 4 and $7{\cdot}\dot{6}$ and of 4 and 3·7 respectively. On this view, therefore, we have three basis constants of benzene, namely, 3·7, 4·0, and $7{\cdot}\dot{6}$, which explain the two most characteristic bands of benzene. Other combinations of these basis constants can be made as follows: $24 \times 7{\cdot}\dot{6} = 46 \times 4 = 184$, which is the wave-number corresponding to $\lambda = 5{\cdot}43\mu$, a value exceedingly close to 5·5 at which Coblentz found a strong band. Again, we have $60 \times 7{\cdot}\dot{6} = 115 \times 4 = 460$, which is the wave number of $\lambda = 2{\cdot}174\mu$ and clearly corresponds to Coblentz's measurement of $2{\cdot}18\mu$. Further, 2×148 (the wave-number of $\lambda = 6{\cdot}75$) $= 296$ corresponding to $3{\cdot}37\mu$, which in all probability is hidden in the great band at $3{\cdot}26\mu$; $3 \times 148 = 444$ corresponds to $2{\cdot}25\mu$, which is hidden in the great band at $2{\cdot}18\mu$, but $4 \times 148 = 592$, which corresponds to $\lambda = 1{\cdot}68\mu$, the value obtained by Coblentz.

These three basis constants therefore explain all the important infra-red bands of benzene except those at $\lambda = 9{\cdot}78$ and $\lambda = 2{\cdot}48\mu$, the remainder being exhibited either at the lowest common multiple of two of the basis constants, or some multiple of it, or at some frequency which is a multiple of two of the constants. As regards the band at $\lambda = 2{\cdot}48\mu$, it is somewhat remarkable that the narrow absorption lines composing the ultra-violet band group of benzene can all be arranged symmetrically round the wave-number 4050 as centre. This number is 10×405, which latter is very near the reciprocal of $2{\cdot}48\mu$. Now no combination of the above three basis constants gives a number near this value; and since this value appears to be a fundamental one for benzene it is in all probability due to there being a fourth basis constant, 10·125. The lowest common multiple of 4 and 10·125, which is 405, gives a wave-length of $2{\cdot}47\mu$, which is exceedingly near to Coblentz's value of $2{\cdot}48\mu$. We are, therefore, left with the band at $\lambda = 9{\cdot}78\mu$, which, however, does not seem to be a specially characteristic band of benzene in spite of its intensity, since it does not evidence itself with any definiteness in benzene derivatives. It is most probable that this band and the remainder of less intensity are due to multiples of the basis constants which happen to fall near together with the result that their effectiveness as absorbers is enhanced. Thus $10 \times 10{\cdot}125$ gives $\lambda = 9{\cdot}88$ and $28 \times 3{\cdot}7 = 9{\cdot}65\mu$, and the mean of these is $9{\cdot}76\mu$."

According to Baly's extension of Bjerrum's theory, all the absorption lines of benzene in the ultra-violet can be calculated from—

$$4050 \pm n \times 3{\cdot}7,\ 4050 \pm n \times 4{\cdot}0,\ 4050 \pm n \times 7{\cdot}\dot{6},\ \text{and}$$
$$4050 \pm n \times 10{\cdot}125.$$

Baly calculated the wave-lengths of the absorption lines of benzene from the above formulæ, and there are about 600 between the limits experimentally observed by Hartley.

The following table gives the results for the first few lines on both sides of the central line, together with the values observed by Hartley and by Grebe (*Zeit. wiss. Phot. IX.* p. 130 (1911)).

Ultra-violet Absorption Band of Benzene.

$K_1 = 3·7$, $K_2 = 4·0$, $K_3 = 7·\dot{6}$, $K_4 = 10·125$.

Red Side.							Blue Side.		
λ Observed.		λ Calc.	n_1	n_2	n_3	n_4	λ Calc.	λ Observed.	
Grebe.	Hartley.							Hartley.	Grebe.
2468·3	2469	2468·4	0	0	0	0	2468·4	2469	2468·3
—	—	2470·7	1	—	—	—	2466·2	2466	2466·5
2471	—	2470·9	—	1	—	—	2466·0	2465	—
—	2472	2472·9	2	—	—	—	2463·9	2464	—
—	—	2473·1	—	—	1	—	2463·7	—	—
—	—	2473·4	—	2	—	—	2463·6	2463	—
2474·5	2474	2474·7	—	—	—	1	2462·3	2462	2462·9
—	—	2475·2	3	—	—	—	2461·7	—	—
2476	2476	2475·8	—	3	—	—	2461·1	2461	—
—	2477	2477·5	4	—	—	—	2459·4	2460	—
—	—	2477·8	—	—	2	—	2459·1	2459	—
2478·6	2479	2478·2	—	4	—	—	2458·7	—	—
2480	2480	2479·7	5	—	—	—	2457·2	—	2457
2481·1	2481	{ 2480·7	—	5	—	—	2456·3 }	2456·5	2456
		{ 2480·8	—	—	—	2	2456·2 }		
—	2482	2482·0	6	—	—	—	2455·0	2455	—
—	—	2482·5	—	—	3	—	2454·5	—	—
2483	2483	2483·2	—	6	—	—	2453·5	2454	2454·0
2484·7	2484	2484·3	7	—	—	—	2452·8	2453	—
—	2485	2485·6	—	7	—	—	2451·5	2452	—
—	2486	2486·6	8	—	—	—	2450·4	2451	—
—	2487	2487·1	—	—	—	3	2450·1	2450	—
—	—	2487·3	—	—	4	—	2449·9	—	—
2488·3	—	2488·1	—	8	—	—	2449·1	—	—
—	2489	2488·9	9	—	—	—	2448·3	2448	2448·5
—	2490	2490·6	—	9	—	—	2446·7	2447	—
2491	2491	2491·2	10	—	—	—	2446·1	2446	—
—	2492	2492·0	—	—	5	—	2445·3	—	—
—	2493	2493·1	—	10	—	—	2444·3	—	—
2493·7	2494	{ 2493·4	—	—	—	4	2444·0 }	2444	2443
		{ 2493·5	11	—	—	—	2443·9 }		
—	2495	2495·6	—	11	—	—	2441·9	—	—
2496·3	2496	2495·8	12	—	—	—	2441·7	—	—
—	2497	2496·8	—	—	6	—	2440·7	2440	2440·6
—	2498	2498·0	13	12	—	—	2439·5	2439	—
2499·1	2499	2499·5	—	—	—	5	2438·0	—	2437·8
—	—	2500·0	14	—	—	—	2437·3	—	—
2501	2501	2500·6	—	13	—	—	2437·1	2437	—
—	2502	2501·6	—	—	7	—	2436·2	—	—
—	—	2502·7	15	—	—	—	2435·0	—	2435
—	2503	2503·0	—	14	—	—	2434·8	2334	—
2504·4	2505	2505·1	16	—	—	—	2432·8	2433	—
		2505·6	—	15	—	—	2432·4	—	—

Baly considers that there is very good agreement between the observed and calculated values. Hartley only records about 300 lines, whilst Baly calculates about 600. Baly

observes that it is obvious from Hartley's paper that more lines exist than those he definitely gives.

Baly also calculated the basis constants for phenol and aniline, and from these constants the wave-lengths of the absorption lines of these substances in the ultra-violet. With regard to phenol he observes, "the number of lines calculated is so large that the agreement between these and the observed values might be criticised as being no better than the theory of probability would give." With regard to aniline, the agreement between observed and calculated values is stated to be very good.

Miss Lowater having measured with very great accuracy the wave-lengths of the absorption lines in a part of the ultra-violet spectrum of sulphur dioxide gas at low pressure (*Astrophysical Journal*, *31*, p. 311, 1910), Baly took the opportunity of submitting his theory to a severe test by calculating these lines by means of his theory and comparing the calculated values with those determined experimentally by Miss Lowater. He decided that there were three basis constants for sulphur dioxide, viz., 2·73, 4·32 and 8·177.

The central line for the group of absorption lines examined by Miss Lowater is $33751{\cdot}6 = 350 \times 2{\cdot}73 \times 4{\cdot}32 \times 8{\cdot}177$.

The heads of the sub-groups are given by—

$$33751{\cdot}6 \pm p \times 2{\cdot}73 \times 8{\cdot}177$$

and the lines in any sub-group are given by—

$$c \pm n \times 2{\cdot}73,$$

where c is the frequency of the central line of the sub-group.

From Miss Lowater's observations it was ascertained that there were seven sub-groups on the less refrangible side of the central sub-group and 13 on the more refrangible side. In each sub-group there were 44 lines on the less refrangible side of the centre and 37 on the more refrangible side.

Baly, therefore, decided on the formula—

$$(350 \times 2{\cdot}73 \times 4{\cdot}32 \times 8{\cdot}177) + (p \times 2{\cdot}73 \times 8{\cdot}177) + (n \times 2{\cdot}73),$$

where $p = -7, -6, \ldots . 0 \ldots . +12, +13$

and $n = -44, -43, \ldots . 0 \ldots . +36, +37,$

from which to calculate the absorption lines.

He calculated 1722 lines as against 586 observed by Miss Lowater, but remarks that no doubt more lines would be observed by a still further improvement of experimental conditions. The agreement between the observed and calculated values is stated to be exceedingly good. The difference in the wave-numbers of any two consecutive lines in the spectrum is 2·73, and this is not much more than twice Miss Lowater's maximum experimental error, and therefore the difference between any observed line and the nearest calculated line cannot be much greater than the maximum experimental error. But the agreement between the observed and calculated values is stated to be on the average much better than this, and is considered to give great support to the formula.

It is noted that the interval between any consecutive pair of observed lines is never less than that calculated from the theory.

These views on the connection between absorption bands in the infra-red and those in the visible and ultra-violet parts of the spectrum are intimately connected with ideas advanced by Baly on what he terms the opening-up of the electric force fields of molecules. The idea was first suggested by some observations made in conjunction with Miss Marsden on the absorption spectra of amino-aldehydes and amino-ketones (*Chem. Soc. Trans.* 1908, *93*, 2108). When an alcoholic solution of such a substance is treated with a small quantity of acid (less than a molecular equivalent) a new absorption band of greater wave-length is developed which causes the solution to become yellow. The addition of more acid forms the ordinary salt, which has almost the same absorption spectrum as the original amino-aldehyde or ketone, and the yellow colour disappears. The position of the new band formed on the addition of a small quantity of acid is the same as that of the fluorescence band of the amino-aldehyde or ketone. Following up this idea, Baly and Rice (*Chem. Soc. Trans.* 1912, *101*, 1475 *et seq.*) found that *o*- and *p*-nitroanisole in sulphuric solution showed bands of greater wave-length than those exhibited in alcoholic solution, and

that these bands disappeared when the substances became sulphonated. Nitroquinol dimethylether, anisole, resorcinol dimethylether and quinol dimethylether behaved in a similar way, and in the cases of anisole, resorcinol dimethylether and quinol dimethylether the bands of greater wave-length exhibited in sulphuric acid solution occupied more or less the same positions as the fluorescence bands of these substances.

The same observers (*Chem. Soc. Trans.* 1913, *103*, 2085 *et seq.*) found that trinitrobenzene exhibits in alcoholic sodium ethoxide solution two bands of greater wave-length in addition to that shown in alcoholic solution; in dimethyl aniline solution also two less refrangible bands, one having the same wave-length as the least refrangible band in sodium ethoxide solution, and the other being still less refrangible. In a mixture of benzene and anthracene it shows a band of wave-length intermediate between the two least refrangible bands in sodium ethoxide solution. Trinitro-anisole and picric acid showed similar behaviour.

The absorption maxima of the bands developed are given in the table—

	4	3	2	1
Trinitrobenzene . . .	600	515	430	— $\mu\mu$
Trinitroanisole . . .	—	510	410	360 $\mu\mu$
Picric acid . . .	—	516	408	359 $\mu\mu$

The frequency difference between successive bands is approximately the same.

In a *résumé* of the subject (Baly, *Jour. Soc. Dyers and Colourists*, 1915, pp. 39 *et seq.*) two further examples are given of constant frequency difference between successive absorption bands, viz., β-naphthol methyl ether shows three absorption bands in alcoholic solution, and also two fluorescent maxima. The values of the frequencies ($1/\lambda$) for these five bands are 2395, 2717, 3044, 3697, and 4350, of which the first two are the fluorescence bands. The differences between consecutive frequencies are very nearly either 327 or 2 × 327.

Again phenol in alcoholic solution exhibits two absorption bands in the ultra-violet region, and in the presence of sodium hydroxide it also exhibits two absorption bands, which, however, are nearer to the red. The frequency difference between these four bands is about 160 units.

Baly's interpretation of these phenomena is that any molecule of a substance in the free state is the centre of a closed field due to the condensing together of the force lines arising from the free affinities of the individual atoms within the molecules. These condensed fields may be unlocked or opened by their interpenetration by the force lines arising from the residual affinity of the molecules of a second substance when the two are mixed. By the residual affinity is meant the balance of free affinity after the maximum possible condensation has taken place.

It follows from the general conception that the opening-up process will be carried out in stages. Baly considers it follows from Planck's quantum theory that there will be a constant frequency difference between the absorption bands corresponding to successive stages in the opening-up process.

Later he was led to detect a relation between this constant frequency difference and the frequency of a band in the infra-red, the frequencies of all the bands in the visible and ultra-violet being integral multiples of the frequency of the vibration causing the infra-red band.

It is rather difficult to criticise this mass of interwoven theories. It must be freely acknowledged, in the first place, that Baly has been able to calculate in a marvellous manner the wave-lengths, or frequencies, of the large number of fine absorption lines exhibited by benzene, sulphur dioxide, etc.

But the theory, or group of theories, has become so elaborate that Baly has now ample expedients at his disposal to account for a band in any position for any substance. All the observed bands can be easily accounted for and as many more as may subsequently be discovered. This is to some extent due to our ignorance of the infra-red absorption spectra of the majority of organic substances.

However, Baly appears to consider the simplest part of

his theory sufficient to account for all ordinary absorption bands (as distinguished from the finer bands observed in vapours under reduced pressure). He lays great stress on the constant frequency difference between successive absorption bands which he has observed for so many substances. In one of his papers (*Phil. Mag.* 1916, *31*, p. 425) he claims: "The existence of these constant differences has now been proved for so many compounds, that the relationship may finally be accepted as absolute." This means that he is content to assert that the frequencies of all the ordinary absorption bands of any substance are integral multiples of the frequency of *one* infra-red band. The later developments of his theory would allow him to call to his aid two or more infra-red bands, but apparently he regards *one* as in all cases sufficient. He may be attacked on the position which he has himself taken up. He has committed himself to the view that the absorption maxima of the various salts of diphenylvioluric acid examined by Hantzsch correspond to different stages in the opening-up of the force-field of this substance (*Jour. Soc. Dyers and Colourists, loc. cit.*). Consequently there must be the usual constant frequency difference between them. The polygenetic dyes, such as the polyhydroxyanthraquinones, are very similar to diphenylvioluric acid, and we may try the application of Baly's theory to these, *e.g.* to alizarin. Meyer and Fischer recorded the positions of absorption bands in sulphuric acid and in alkali. (Baly might apply some correction to these bands on account of the solvents in which they were observed, but he has given no rules as to the magnitude of these corrections, and from his examples it appears that they are too small to affect the present argument.) Watson and Meek (*Chem. Soc. Trans.* 1915, *107*, 1574–6) tried to calculate the fundamental frequency from these figures, and also to what integral multiples the observed bands corresponded (figures are $1/\lambda$ in the usual units divided by 10)—

(Expt.)	160 162	180 193	200	303 312	372 376 385
(Calc.)	162	189	202	310	378
(Calc.)	13·5 × 12	13·5 × 14	13·5 × 15	13·5 × 23	13·5 × 28

A fundamental frequency of about $7·4\,\mu$ would satisfy requirements, but we have to regard one of the absorption bands as the 28th multiple of this fundamental frequency. It would seem natural to expect, if bands in the visible and ultra-violet are harmonics or overtones of fundamental frequencies in the infra-red, that the simpler multiples, 2, 3, 4, etc., would be much more prominent than the higher multiples. Yet even in the cases interpreted by Baly himself the simpler multiples are rarely observed. The various benzene bands are regarded as the 6th, 9th, and 10th multiples of the fundamental frequency, whilst for *p*-xylene he has to go as high as the 15th multiple. Here we have to go further still—up to the 28th multiple.

Watson and Meek (*Chem. Soc. Trans.* 1916, *109*, 556) subsequently considered the alizarin bands observed in alcoholic solution and in dyeings on chrome, alum and tin mordants, and found that these did not correspond to any integral multiples of the fundamental frequency 135. To include them in the series it was necessary to halve the fundamental frequency and regard one of the absorption bands as the 57th multiple.

(Expt.)	160–162	180	192–193	198–200	213
(Calc.)	162	175·5	189	195·75	209·25
(Calc.)	6·75 × 24	6·75 × 26	6·75 × 28	6·75 × 29	6·75 × 31

(Expt.)	223	303	312	372	376	385
(Calc.)	222·75	303·75	310·5	371·25	378	384·75
(Calc.)	6·75 × 33	6·75 × 45	6·75 × 46	6·75 × 55	6·75 × 56	6·75 × 57

And there can be no doubt that if other salts were examined, such as the calcium, strontium and barium salts, additional maxima would be obtained, and this would involve still further reduction of the fundamental frequency with corresponding increase of the integral multiples. To the mind of the present writer this would be a *reductio ad absurdum*. The fundamental frequency would become so low as to be out of the ordinary field of observation, and the integral multiples would rise to enormous figures. Moreover, there are very distinct limits to the accuracy obtainable in determining the positions of absorption maxima owing to the

indefiniteness of the bands, and if the fundamental frequency were taken any lower than 67·5 the experimental error in determining the position of any absorption band would be greater than the distance between successive multiples of the fundamental frequency, and consequently a band in any position whatever might claim to fit into the series.

But even if Baly's theory were established it would lead to no conclusions as to the relation between chemical constitution and colour. We have already mentioned that the theory, or theories, could account for an absorption band in any position whatever for any substance. As a matter of fact any particular substance exhibits a very limited number of absorption bands under any particular conditions, and we want to be able to calculate the positions of these bands from the constitutional formula of the substance. Baly would say, for example, that the shade of dyeing obtained with alizarin on alum mordant corresponds to a particular stage in the opening-up of the force-field of alizarin, and this corresponds to the 29th multiple of a fundamental frequency of 67·5. It is possible that the fundamental frequency of 67·5 might be referred to some radicle in the alizarin molecule, but there is no explanation whatever as to why this particular infra-red vibration, rather than any of the others executed by alizarin, should be *the* one to give harmonics or overtones. Still less is there any explanation as to why the 29th multiple, rather than the 28th or 30th or *m*th or *n*th multiple should be called up when the alizarin is fixed on alum mordant.

Before it could be of any use in explaining the colours of substances under definite conditions, or predicting the colours of substances which might be synthesised, it would be necessary to know (1) the relation between constitution and positions of the absorption bands in the infra-red; (2) which bands in the infra-red would have correlated bands in the visible and ultra-violet; (3) which integral multiples of the frequency of the infra-red band would represent the bands which appear under certain conditions, *e.g.* why in the case of *p*-xylene we have 257×8, 257×10, 257×14, and 257×15, but not 257 multiplied by 5, 6, 7, 9, 11, 12 or 13; and why the

multiple 8 should be prominent for cathodo-luminescence, 10 for phosphorescence, 14 for fluorescence and 15 for absorption.

MOLECULAR AGGREGATION MAY HAVE AN INFLUENCE ON THE COLOUR OF ORGANIC SUBSTANCES

We are well acquainted with the idea that the state of aggregation may have an influence on the colour of a substance. The red and yellow varieties of mercuric iodide are generally considered as different polymeric forms. The red and black modifications of mercuric sulphide are similarly explained. The different colours exhibited by colloidal silver solutions are considered to be due to the scattering of light by the molecular aggregates which are large enough to be detected in the ultra-microscope.

The colours exhibited by most organic dye-stuffs and coloured compounds under ordinary conditions cannot be regarded as due to scattering of light by the particles, since most of them show normal molecular weight in solution. But in a comparatively few cases the colour is probably influenced by the state of molecular aggregation. Vogel (*Berl. Mon. Ber.* 1878, 409–431) pointed out that some dye-stuffs in the solid state have quite different absorption spectra from those exhibited by their solutions. The present writer has observed that the alkali salts of alizarin and other poly-hydroxyanthraquinones show little selective absorption in the solid state. Hantzsch (*Ber.* 1909, *42*, 68) has shown that the colour of N-methylphenylacridonium iodide is influenced by the state of molecular aggregation. In aqueous solution it is monomolecular and yellow, whilst in chloroform it is trimolecular and brown. Piccard (*Ann.* 1911, *381*, 351 *et seq.*) has shown that Würster's salts can be obtained in two modifications which he terms α- and β-. The series of α-compounds shows the well-known deepening of colour from yellow to orange, red, violet and blue by progressive methylation. The β- modifications show deeper colours and quite different absorption spectra (Fig. 60).

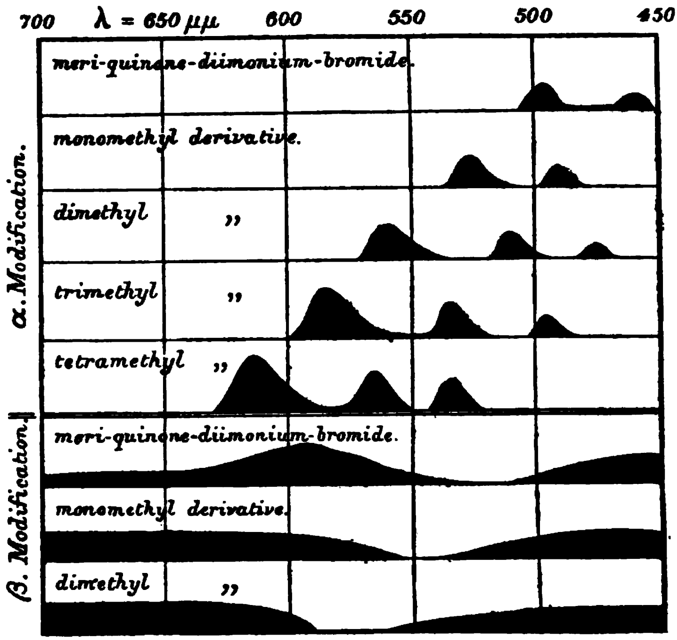


FIG. 60.

Absorption spectra of the meri-quinone diimonium salts.

(Reproduced from Piccard's paper, *Ann.*, 1911, 381, p. 354.)

This is explained as due to the state of molecular aggregation.

CHAPTER VII

INFRA-RED ABSORPTION SPECTRA OF ORGANIC SUBSTANCES

PROBABLY no justification is needed for including in this volume a short account of the infra-red absorption spectra of organic substances. It has been already pointed out that it would be unwise to confine our attention exclusively to the visible spectrum in our attempts to find out relations between colour and constitution, and to discover the nature of the vibrations responsible for visible colour; and in the preceding chapters reference has frequently been made to the ultra-violet absorption of dye-stuffs and the substances of which they may be regarded as derivatives. It would appear only logical to pay some attention also to the infra-red spectra of these substances. Some account has already been given of Baly's theory, according to which absorption bands in the visible and ultra-violet are connected with fundamental vibrations in the infra-red, and it would be impossible properly to estimate the value of this theory without some idea of the general nature of the absorption of infra-red rays by organic substances.

It may, however, be said at once that the infra-red absorption spectra of dye-stuffs and their parent substances are as yet unexplored, and the same may be said of coloured organic compounds in general. Attention has been devoted up to the present to simpler substances, such as water, ammonia, hydrochloric acid, carbon monoxide, carbon dioxide, nitrous oxide, hydrocarbons, alcohols, phenols, amines, simple acids, esters, etc. Some essential oils and a number of alkaloids seem to be the only complicated organic compounds which have been examined.

The fact which stands out most prominently is that nearly

all the substances which have been examined exhibit selective absorption in the infra-red, and most substances, even the simplest, show a large number of absorption bands. If we reflect that the ultra-violet portion of the spectrum to which attention has hitherto been directed extends from about 0·25 to 0·45μ, and the visible from 0·45 to 0·75μ, whilst the infra-red spectrum can already be examined up to 350μ, we feel somewhat as a geologist might who, having hitherto confined himself to the British Isles, suddenly obtained access to the rest of the globe, and was made aware of the relative proportions of the old and new areas for investigation; or as an astronomer who had hitherto confined himself to the solar system, when his attention was first directed to other heavenly bodies. As already mentioned, we have no data for comparing the infra-red spectra of dye-stuffs and coloured compounds with those of simple substances, such as water, the hydrocarbons, alcohol, etc.; and under the circumstances it would be obviously very unwise to form any opinion as to the help we are likely to get from the infra-red region for our studies on visible colour. But at first sight the fact that so many simple substances exhibit a wealth of detail in their infra-red spectra, and no bands in the visible and ultra-violet, would seem to indicate that there is no very obvious connection between the new and old fields of investigation.

The first study of absorption spectra of organic substances in the infra-red was made by Abney and Festing (*Phil. Trans.* 1881, *172*, III, 887–918). The region investigated was from 0·78 to 1·2μ—a very small region compared with the field which is now open for examination. But the examination, even of this restricted area, revealed a wealth of detail in the spectra of most substances, including the simplest, such as the fatty alcohols, aldehydes and acids, alkyl halides, etc. Fig. 61 shows the spectra in this region of some of these substances.

Abney and Festing put forward a view, with reference to the bands they observed, which has been adopted by all subsequent workers in the infra-red regions and held to apply to bands in the much wider fields examined by them: viz., that characteristic organic radicles have corresponding character-

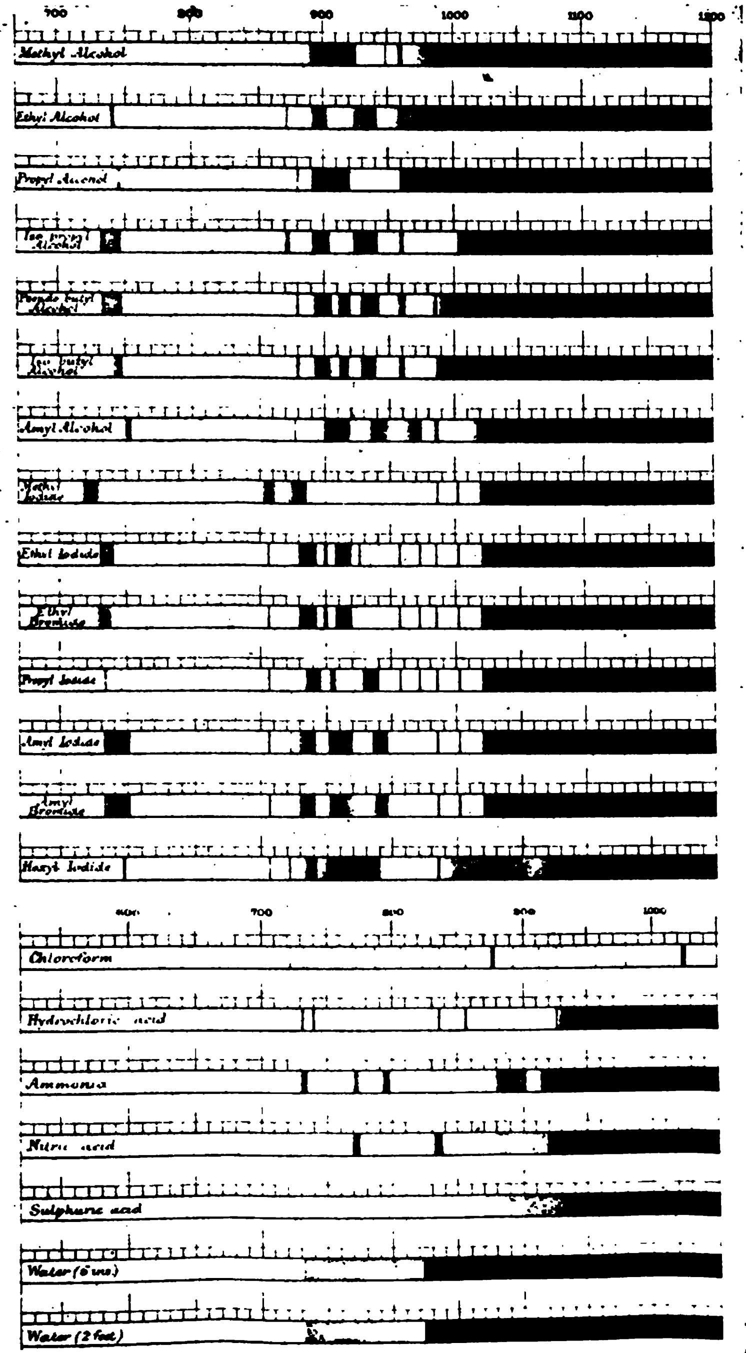


FIG 61.

Infra-red absorption spectra.

(Reproduced from Abney and Festing's paper, *Phil. Trans.*, 1881, 172, III, Plate 86.)

istic absorption bands. They considered that the bands (or lines) are primarily due to hydrogen combined with carbon, as compounds such as carbon tetrachloride and carbon disulphide show no bands in this region. They regarded the bands (or lines) in the region 1·0 to 1·1μ as characteristic of the radicles, whilst those occurring between 0·7 and 1·0μ were regarded as depending on the arrangement of the molecule. A very characteristic group of bands between 1·0 and 1·1μ will be found in the spectra of propyl-, pseudobutyl-, and amyl-alcohols, also in methyl-, ethyl-, propyl-, amyl-, and hexyl-iodides, ethyl and amyl bromides, diethyl ether and amyl nitrite. These might be regarded as characteristic of the CH_2 group were it not for the fact that they do not all occur in methyl alcohol, acetaldehyde, acetic acid, ethyl nitrate, ethyl sulphide, amyl ether, or dimethylaniline. Benzene, phenyl bromide, and benzyl chloride show another characteristic group of bands in this region; but this group has disappeared from the spectra of aniline, dimethylaniline, nitrobenzene, phenylpropyl alcohol, benzyl ethyl ether, and ethyl benzoate.

Julius (*Arch. Neerland,* 1888, *22*, 310–383; *Verhand. k. Akad. v. Wette,* Amsterdam, 1892, *1*, 1, 1–49) extended the field of observation, and concluded that alkyl radicles gave bands at 0·8 to 0·9μ and at 3·45μ.

Donath (*Wied. Ann.* 1896, *58*, 619–661) found that uranin, eosin, fluoresceïn, aesculin and chlorophyll showed no absorption from 0·7 to 2·7μ, apparently disproving the idea of any absorption in this region due essentially to the benzene nucleus or correlated with colour or fluorescence.

Puccianti (*Nuovo Cim,* 1900 (4) *11*, 241–278) found a band at 1·71μ in thirteen compounds in which hydrogen was connected with carbon; he considered bands at 2·18 and 2·49μ characteristic of benzene and benzene derivatives; and a band at 2·1μ characteristic of alcohols.

Iklé found that all the substances examined exhibited a band at 3·24 to 3·44μ. (*Ueber das ultrarothe Absorption-spectrum einiger organischer Flüssigkeiten,* Dissert, Berlin, 1903. Lütcke und Wulff, Hamburg).

Coblentz has more recently made an examination of infra-red absorption spectra up to 15μ (*Astrophys. Jour.* 1904, *20*, 207 *et seq*; *Publications of the Carnegie Institution*,

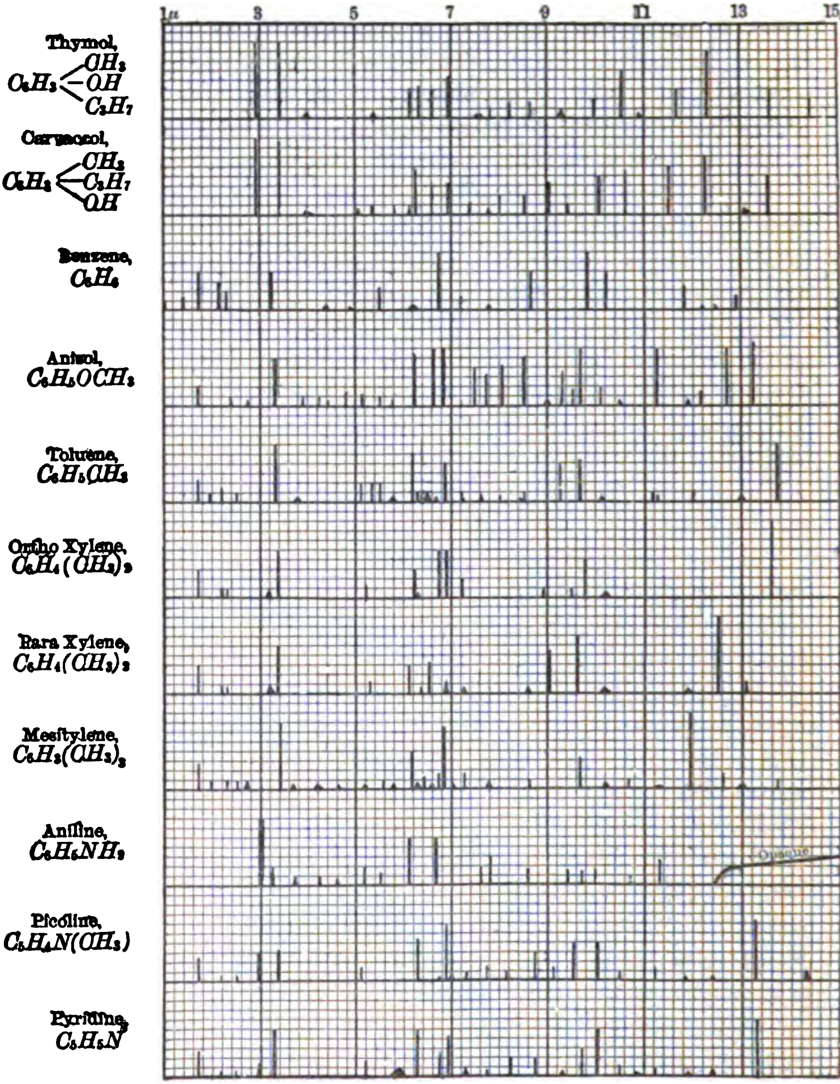


FIG. 62.

(Reproduced from Coblentz's paper, *Astrophys. Jour.*, 1904, **20**, p. 220.)

Washington, No. 35 (1905). Some idea of the general character of the absorption spectra obtained may be formed from an examination of Figs. 62 and 63.

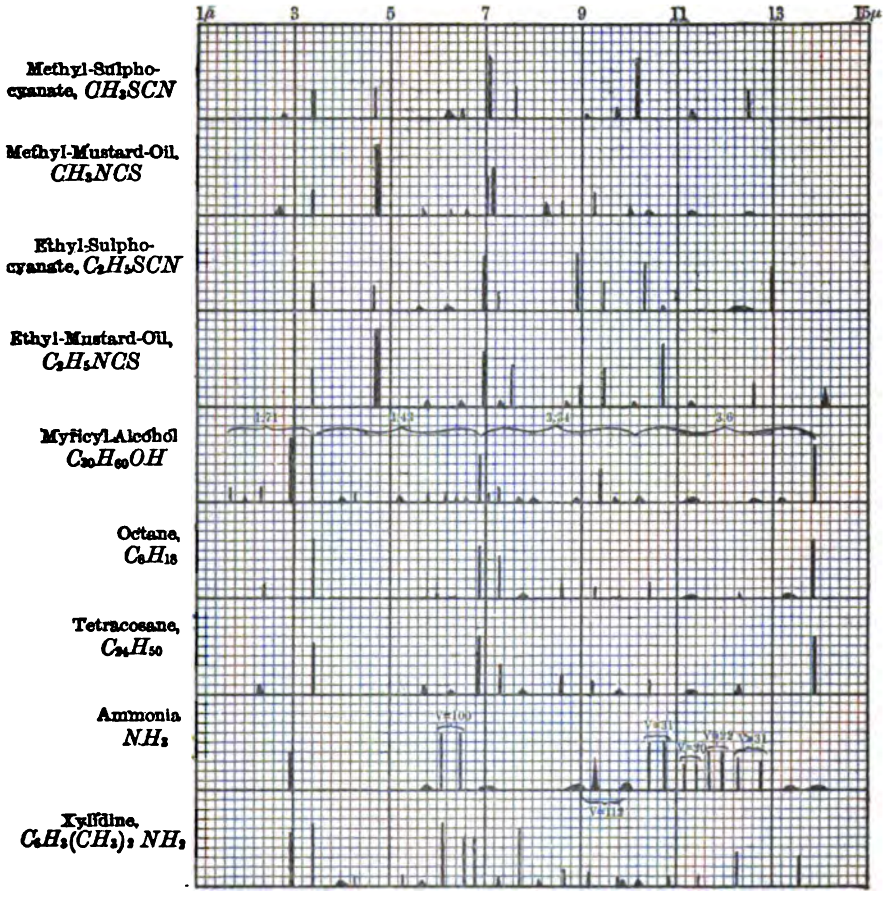


FIG. 63.

(Reproduced from Coblentz's paper, *Astrophys. Jour.*, 1904, 20, p. 222.)

Coblentz finds a band at 1·71μ in all compounds where H is attached to C. He finds a band at about 3μ in many organic substances, including alcohols, phenols, aniline, and pyridine; and also in water and ammonia; he finds a band at 3·43μ in methyl and ethyl iodides, nitrates and cyanides,

toluene and myricyl alcohol; but it cannot be regarded as entirely characteristic of the methyl group, as it also occurs in aniline.

Two paraffins, octane C_8H_{18}, and tetracosane, $C_{24}H_{50}$, despite the great difference in molecular weight, showed identical spectra, the bands occupying the same position to within 0·03μ. *All* the prominent lines found in these spectra were found in the spectra of each of twenty-five hydrocarbons of the formulæ C_nH_{2n+2}, C_nH_{2n}, and C_nH_{n-2} as well as

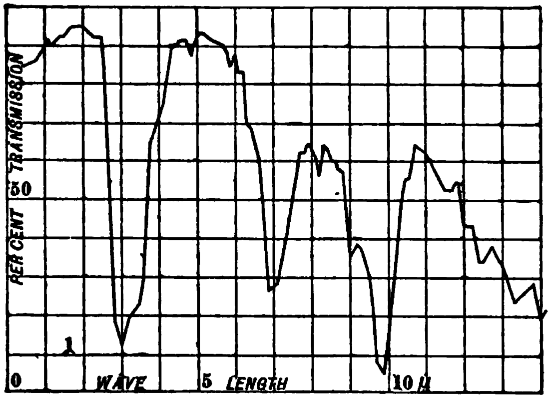


FIG. 64.

Methyl alcohol.

(Reproduced from Weniger's paper, *Physical Review*, 1910, Curve 1 in Plate facing p. 420.)

in many other compounds such as myricyl alcohol and piperidine.

In the absorption spectra of many substances a series of bands are found which appear to be harmonics: *e.g.* Aschkinass (*Annalen der Physik*, 1895, *55*, 401) found bands for water at 1·51, 3·06 and 6·1μ; Rausohoff (*Inaugural Dissertation*, Berlin, 1896) found for alcohols the harmonics 1·71 and 3·43μ; also 3 and 6·06μ; Coblentz for myricyl alcohol 1·71, 3·43, 6·86, 10·2 and 13·88μ; also 2·95 and 5·8μ; for benzene we have bands at 1·68, 3·25, 6·75, and 9·8μ.

Weniger (*Physical Review*, 1910, *31*, 388 *et seq.*) has studied the absorption spectra of a large number of fatty

alcohols, acids and esters, and has recorded his results in curves similar to the generally adopted absorption curves for the visible and ultra-violet regions (Fig. 64).

He comes to the conclusion that the following groups and bands are related :—

OH in alcohols, 3·0 and 6·9μ.

CH_2 in alcohols, acids, and esters, 3·4μ.

CH_2 in esters and higher alcohols, 7·3μ.

C = O, 5·9 and 8·2μ.

In addition to these, many other bands were observed, but they could not be attributed to special atomic groups.

Finally, we may mention the isolated investigation of the infra-red absorption spectra of two dye-stuffs, fuchsine and cyanine (Coblentz, *Phys. Rev.* 1903, *16*, 119–122). Cyanine has a strong double band which begins at 5·5μ and extends to 9·5μ.

Dr. Eva von Bahr (*Phil. Mag.* 1914, *28*, VI, 71 *et seq.*) finds that carbon monoxide, carbon dioxide, and nitrous oxide, in the form of gas at low pressures, exhibit double bands in the region from 4 to 5μ. In the case of carbon dioxide the two maxima are about 0·1μ apart, and in the other cases less. Earlier observers had found that hydrochloric acid gas at ordinary pressure exhibited two absorption maxima at about 3·4 and 3·57μ. Dr. Bahr has succeeded in resolving these into narrower bands (seven in the one case and five in the other). She shows that these narrower bands can be calculated from bands of very low frequency, which Rubens has observed in the region from 100 to 350μ (Rubens and v. Wartenberg, *Verh. d. Deutsch phys. Ges.* 1911, *13*, 796), and which perhaps correspond to the periods of rotation of the molecules. Similar bands have been found for water vapour in the region from 50 to 100μ, and minor bands on each side of the water vapour band at 6·3μ can be deduced from them in a similar manner.

CHAPTER VIII

FLUORESCENCE

THE phenomenon of fluorescence is too well-known to need description. When ordinary white light falls on a fluorescent substance it emits coloured light, so that for certain wave-lengths the intensity of the reflected is apparently greater than that of the incident light. Sir George Stokes was one of the early investigators of fluorescence. He showed that certain select rays of the white light are absorbed, *i.e.* the fluorescent substance exhibits selective absorption, and utilises part of the energy of the absorbed rays to generate light of greater wave-length. Stokes's Law states that the emitted waves have a longer period than those which are absorbed.

Relation between the wave-lengths of the absorbed and emitted rays.—It has just been mentioned that the wave-length of the emitted is greater than that of the absorbed light. Baly has sought to establish a relation between these wave-lengths, which has already been indicated in the account of his theory, according to which the wave-lengths of the maxima of absorption can be calculated from a fundamental vibration period in the infra-red. The substance may absorb or emit light of which the frequency is any integral multiple of this fundamental frequency. The more the electric force-field of the molecule is opened up, by solution or chemical combination or incipient chemical combination, the lower are the integral multiples of the light which may be absorbed or emitted. It appears that the emitted light is generally ahead of the absorbed light, *i.e.* the emitted light has a frequency which is a lower integral multiple of the fundamental than the absorbed light.

In several cases it has been shown that the light which is emitted by a substance in one solvent has the same period as an absorption band exhibited by the same substance in another solvent.

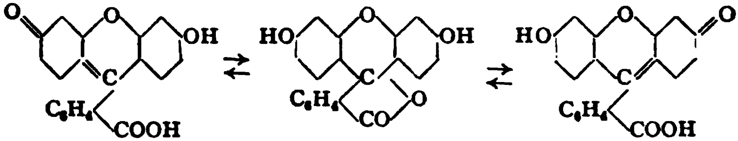
This explains a very common phenomenon in connection with fluorescence, viz. that the same substance will fluoresce with different colours in different solvents. Kauffmann pointed out (*Ber.* 1908, *41*, 4396) that the change in colour of fluorescence on change of solvent follows the same order as the change of colour itself. The fluorescent band of the solid substance lies farthest towards the ultra-violet, then follow the solutions in indifferent solvents, then those in dissociating solvents. According to Baly's theory the fluorescence continues a phase ahead of the absorption.

Ultra-violet fluorescence.—Stark and Meyer (*Physik. Zeit.* 1907, *8*, 250) have shown that many substances exhibit fluorescence in the ultra-violet. This is a fact of great importance, which will probably lead to the abandonment of theories as to the relation between constitution and fluorescence which have been based only on naked-eye observations.

RELATIONS BETWEEN CHEMICAL CONSTITUTION AND FLUORESCENCE

Hewitt's Theory (*Chem. Soc. Proc.*, 1900, *16*, 3).—According to this theory, fluorescence is due to a particular kind of tautomerism, which Hewitt has termed ***double symmetrical tautomerism***. The theory is almost identical in form with those which explain colour or selective absorption as due to a vibration between different tautomeric forms; or, in those cases where ordinary tautomerism is excluded, as due to an oscillation between forms which can be represented by different valency arrangements in the molecule (isorropesis). According to Hewitt, if this vibration is symmetrical it will cause fluorescence. What is meant by a symmetrical vibration will be made clear by an example. Fluoresceïn, which is a fluorescent substance, may be considered to tautomerise

from the quinonoid form A_1 to the non-quinonoid form B, and then to the quinonoid form A_2.



A_1 B A_2

It can tautomerise back from A_2 through B to A_1 so that we have the cycle—

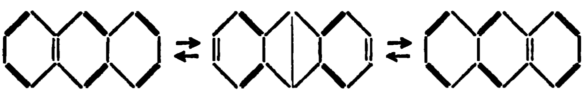
$$\begin{tikzcd} & B \arrow[dr] & \\ A_1 \arrow[ur] & & A_2 \arrow[dl] \\ & B \arrow[ul] & \end{tikzcd}$$

And A_1 and A_2 are identical, except that the two benzene nuclei are taking turn about to become quinonoid.

Symmetrical dimethyl fluoresceïn is also fluorescent for the same reason.

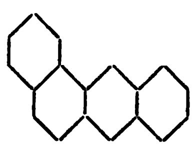
But asymmetrical dimethyl fluoresceïn is not fluorescent.

The fluorescence of anthracene can be explained by a similar symmetrical vibration, although there is no movement of a labile hydrogen atom but only a rearrangement of valencies.

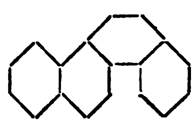


This theory explains why acridine and phenosafranine hydrochloride fluoresce strongly, whilst chrysaniline and aposafranine hydrochloride show only weak effects. The former are symmetrical and the latter asymmetrical.

According to this theory only symmetrical compounds should exhibit fluorescence. It is easy to point out many asymmetrical compounds which fluoresce strongly, *e.g.* naphthanthracene, chrysene, β-anthrapyridine and phenonaphthacridine.

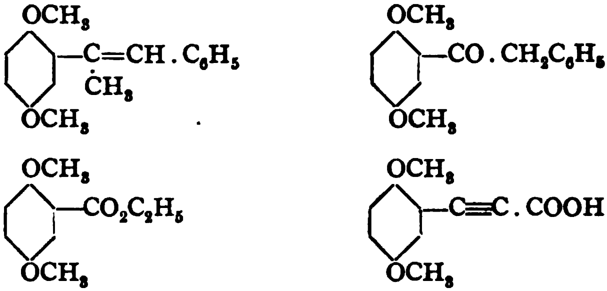


Naphthanthracene.



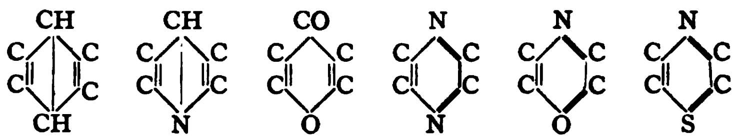
Chrysene.

The following derivatives of the dimethyl ether of hydroquinone, prepared by Kauffmann, are fluorescent; and yet it is not very obvious how there can be any tautomerism or molecular rearrangement; and, in any case, their structure is asymmetrical.



Also it is easy to disprove the theory in the converse way, as there are many compounds capable of such a symmetrical tautomerism, or isorropesis, which do not exhibit fluorescence, *e.g.* symmetrical dinitrofluoresceïn.

Meyer's Fluorophore Theory (*Z. phys. Chemie*, 1897, *24*, 468).—This theory was fashioned after Witt's theory as to the relation between colour and constitution. Corresponding to Witt's chromophore, Meyer postulated a *fluorophore* for the production of fluorescence. He recognised the following ring complexes as fluorophores.



The fluorophore is not in itself sufficient to produce fluorescence. It must be associated with dense atomic complexes before the phenomenon becomes manifest, *e.g.* the addition of benzene nuclei at the sides of the fluorophore produces the requisite complexity and packing and we get fluorescence in anthracene, acridine, xanthone, etc.

The theory does not explain why the introduction of certain atoms or groups into fluorescent substances destroys

fluorescence, *e.g.* chlorine atoms and nitro groups; and why the acetylation of hydroxyl or amino groups has the same effect.

Kauffmann's Theory.—This theory was developed by Kauffmann from his observations on the luminescence of organic substances in the Tesla rays, and forms a companion as it were to his Auxochrome Theory of colour, which also arose from the same observations. An account of these observations will be found in Chapter II (under the head of H. v. Liebig's modification of the quinonoid theory). A benzene nucleus in which the arrangement of bonds is according to Dewar's formula, or approximates to this, is the

cause of luminescence. As already mentioned, the introduction of auxochromes into the nucleus is supposed to cause the bonds to approximate more nearly to this condition and it consequently increases luminescence. A benzene nucleus in this condition is termed a *luminophore.* The luminophore is, therefore, in itself a complex, viz. a benzene nucleus together with the attached groups, nuclei or what not, which cause it to approximate to the above arrangement of bonds. A luminophore can be converted into a fluorescent substance by the introduction of a *fluorogen.* The following groups, etc., are fluorogens, viz. carboxyl, carbonyl, cyan-, the acrylic acid group, the ethylene bond and conjugated ethylene bonds, the benzene ring and *o*- and *p*-quinonoid rings, the azomethine group and the conjugated azomethine ring.

[We may notice here a fundamental difference between Meyer's and Kauffmann's theories. For example, in fluorescein Meyer regards the γ-pyrone ring as the seat of fluorescence; the *fluorophore*, and the fluorescence is made manifest by attaching benzene nuclei to the sides of the pyrone ring, and intensified by the auxochromes. Kauffmann regards the benzene nuclei as the luminophores, their luminescence

being converted into fluorescence by the substituted γ-pyrone ring which he includes under the heading of *p*-quinonoid rings.]

It remains to be explained how it is that a luminophore is not always rendered fluorescent by the introduction of a fluorogen. It appears that the fluorogen is not able to exert its effect equally well in all positions, *e.g.* anthranilic acid is strongly fluorescent, whilst the phenomenon is scarcely exhibited by *p*-amino-benzoic acid. Kauffmann frames empirical rules as to the favourable and unfavourable positions for fluorogens; *e.g.* if two auxochromes and one fluorogen are present together in a benzene nucleus the arrangement must be asymmetrical to produce fluorescence. We have also to take into account the influence of the fluorogen on the arrangement of bonds in the nucleus. We see that some of the fluorogens, *e.g.* the carboxyl group, are negative in character, and tend to throw the benzene nucleus into another condition such as is represented by the Kekulé or the Claus formula, and if this influence is appreciable the luminophore is destroyed or weakened. Finally, the addition of other groups has to be taken into consideration. If these are strongly negative in character they will weaken or destroy the luminophore. This explains why the introduction of a nitro-group almost invariably destroys fluorescence. It will be seen then that Kauffmann's theory has become very complicated. Fluorescence is dependent on (1) the presence of a benzene nucleus (or similar ring); (2) its assuming approximately the arrangement of bonds according to Dewar's formula—this is determined by the total effect of all groups introduced into the nucleus, auxochromes, fluorogens and other groups; (3) the presence of a fluorogen; (4) a favourable arrangement of fluorogen with reference to the auxochromes and other groups present in the nucleus.

This theory may account fairly well for the facts, and give us working rules as to the relation between constitution and fluorescence, but it gives us no idea as to the nature of the vibrations causing the fluorescence. According to Baly's theory, selective absorption and fluorescence are due to the

same vibration, or are derived from the same fundamental vibration; and it remains to be explained why particular integral multiples of the fundamental frequency are chosen for absorption and fluorescence respectively in the individual cases.

Stark's Theory: That all substances possessing selective absorption are fluorescent.—Francesconi and Bargellini (*Atti R. Accad. Lincei*, 1906 [v] 15, ii, 184) advanced the opinion that all aromatic substances are either actually or potentially fluorescent. Since almost all aromatic substances show selective absorption, whilst most fatty compounds do not, there is a close similarity between this view and that expressed by Stark after his detection of fluorescence in the ultra-violet. The demonstration that this phenomenon may be exhibited in the ultra-violet makes it necessary to revise our theories as to the relation between constitution and fluorescence, after our list of fluorescent substances has been revised by the inclusion of those which fluoresce in the ultra-violet. Stark (*loc. cit.*), indeed, advances the view that all substances possessing selective absorption are fluorescent. Such a view is evidently not based on complete experimental evidence, and, indeed, he seems to have examined comparatively few substances for ultra-violet fluorescence. But if this view should be confirmed by experiment it will then follow that the same relation exists between constitution and fluorescence as between constitution and selective absorption. It will then only remain to discover why fluorescence is relatively strong compared with absorption in some substances and relatively weak in others, and what is the relation between the periods of absorption and fluorescence.

In connection with the study of ultra-violet fluorescence it has been shown that substituents influence the position and strength of the fluorescent bands just as they influence the absorption bands. Auxochromes are, therefore, *auxoflores*, and bathychromic groups are *bathoflores*. But since the relative intensity of fluorescence and absorption is not always the same there may be additional auxoflores and additional

bathoflores. Alkyl groups act as auxoflores without shifting the positions of the bands. The following groups intensify the fluorescence and also shift it in the direction of lower refrangibility, viz. OH, OCH_3, NH_2, CN, COOH, CH : CH.

The nitro-group, the halogens, and the azo-group are bathoflores.

CHAPTER IX

THE COLOUR AND SPECTRA OF INORGANIC COMPOUNDS

It is generally considered that the colours of organic and inorganic compounds are due to different causes. This is due to the fact that the simpler compounds of carbon are colourless under ordinary conditions, whereas even the simplest compounds of many other elements are coloured. Most organic compounds consist of carbon and hydrogen, carbon, hydrogen and oxygen, carbon, hydrogen and nitrogen or carbon, hydrogen, oxygen and nitrogen only. Hundreds of organic compounds are known which are colourless under ordinary conditions. This has led to the view that colour when developed in organic compounds is due to some special arrangement of the atoms in the molecule, whereas the colour of simple inorganic compounds is considered to be due to something inside the atoms of the elements forming those compounds—*i.e.* some intra-atomic arrangement or vibration as distinguished from the inter-atomic arrangement or vibration which is supposed to cause the colour of organic compounds.

There are, however, facts which warn us against the unqualified acceptance of this view. On the one hand, we must recognise that even the elements—carbon, hydrogen, oxygen, nitrogen, and their simple compounds—can exhibit colour under certain circumstances. The ordinary forms of solid carbon, viz. charcoal, lamp-black and graphite, are black or grey, which means that they absorb all the rays of the visible spectrum. Oxygen gas appears to be colourless, yet it absorbs rays in the red part of the spectrum and is responsible for a considerable number of bands seen in the ordinary solar spectrum. Liquid oxygen is of a pale blue colour.

Liquid ozone is of a deep indigo-blue colour, which is so intense that a layer 2 mm. thick is opaque. And when stimulated by the electric current or discharge all these elements emit light of characteristic vibration frequencies—*i.e.* give emission spectra containing characteristic lines (or bands), and the light emitted is coloured even to the naked eye. On the other hand we must recognise that there are scarcely any elements, not even those which are generally regarded as coloured elements *par excellence*, which are not colourless under certain conditions. Chromium, manganese, iron, nickel, cobalt, and copper are regarded as the essentially coloured elements, yet the first five of these are white in the metallic condition.* Nor are all their compounds coloured, *e.g.* anhydrous copper sulphate is white.

It is interesting to take a general view of all the elements and their simpler combinations from the point of view of colour development.

In an ordinary way we regard a substance as coloured if a considerable mass of it under ordinary conditions of temperature and pressure absorbs some of the rays of the visible spectrum on reflection or transmission; we cannot disregard colour which may be manifested under other circumstances. Metallic sodium and sodium salts when introduced into a flame emit a yellow light and give a very characteristic emission spectrum consisting of a very sharp double line. Sodium vapour at the same temperature gives an absorption spectrum which is the exact complementary of this emission spectrum, *i.e.* the absorption spectrum consists of a sharp double line occupying exactly the same position as the bright double line in the emission spectrum, so there is obviously some connection between the colour of emitted and absorbed light. At the same time it must be admitted that there is not generally any such obvious connection between the emission and absorption spectra of substances; *e.g.* the absorption bands of iodine vapour are not identical with or even analogous to the bright lines of the emission spectrum.

* This may be only because they reflect the greater portion of the incident light unchanged; but, whatever the reason may be, they are apparently white.

This is because the emission and absorption spectra are usually obtained under different conditions—of temperature, pressure, molecular aggregation, etc. A great deal of attention has been devoted to emission spectra, partly because of their value for the detection of many elements. And it seems as though we are now approaching a knowledge of the cause of these spectra. Yet even when this has been attained we shall probably still be a long way from understanding the cause of absorption spectra and colour as manifested under ordinary conditions.

It is interesting to note that every element is capable of exhibiting colour under appropriate circumstances. The alkali and alkaline-earth metals show very little tendency in this direction. The metals in the solid state, their oxides, chlorides, sulphates, etc., are colourless, yet their vapours are coloured and they all give characteristic flame colorations.

The Emission Spectra of Elements and the Colours imparted to Flames by Metals and Metallic Salts

Considerable success has recently been attained in accounting for the emission spectra of the simplest elements, viz. hydrogen and helium. The positions of the lines can be calculated on the assumption that the hydrogen atom consists of a central nucleus charged with positive electricity, and a negative electron which is rotating round it in an orbit determined by the electrostatic action of the charges and the ordinary laws of motion. The rotational vibration of the electron is the cause of the lines in the emission spectrum (N. Bohr, *Phil. Mag.* 1913 [vi] *26*, 1, 476; 1914 [vi] *27*, 506). A series of lines in the helium spectrum can be explained as due to an atom of the element which has lost one of its two electrons, the rotational vibration of the remaining electron being the cause of the lines of this series.

It seems probable that it will soon be possible in a similar way to account for the emission spectra of other elements.

Already it has been shown that for some series of elements

the positions of corresponding lines in the spectrum shift in a regular manner with change in the atomic weight. Ramage (*Proc. Roy. Soc.* 1902, *70*, 1) constructed a diagram in which the frequency of a line was represented by the abscissa, whilst the ordinate was proportional to the square of the atomic weight of the element in whose spectrum the line was contained. A straight line could be drawn through corresponding points in the diagram for potassium, rubidium, and cæsium. Similarly a straight line could be drawn through a set of corresponding points for calcium, strontium, and barium. [It should, however, be mentioned that lithium and sodium would not fall into the series with potassium, rubidium, and cæsium; also that other sets of corresponding points for calcium, strontium, and barium could not be connected by straight lines.] In both series the frequency of corresponding lines decreased with increase of atomic weight.

Flame colorations are the total effect on the eye of the emission spectra of the metallic elements introduced into the flame, so that in consequence of the above-mentioned regularities we might at first expect to find the flame colorations of potassium, rubidium, and cæsium in the same order as the colours of the spectrum passing from the blue to the red end. We do find that the flame coloration of rubidium is redder than that of potassium, whilst that of cæsium is redder still. But in the case of calcium, strontium, and barium, the colour change is in the reverse direction. As a matter of fact, the spectral lines considered by Ramage are by no means the only lines in the flame spectra of these elements. For example, in the case of calcium he only considers the lines of wave-lengths 4226, 3968, and 3933, which are all outside the visible spectrum. So that the regularity which he observed does not apply to the lines in the orange and yellow to which the characteristic flame coloration of calcium is due. In short, it has been shown that in some series the frequencies of the spectral lines are simple functions of the atomic weights; but sufficient regularities have not yet been observed for us to show how the flame colorations can be calculated from the atomic weights.

The Colours of the Elements under Ordinary Conditions

The only elements possessing marked colour under ordinary conditions are: copper (red), gold (yellow), phosphorus (red in amorphous form), sulphur (yellow), selenium (red), chlorine (yellowish green), bromine (orange-red), and iodine (violet). The number of elements possessing any marked colour is so small that no connection with the atomic weights or periodic arrangement of the elements is obvious.

Absorption Spectra of the Halogens, Sulphur and Oxygen

The absorption spectra of these elements are of special interest, as there seems the possibility that their study may establish the connections between emission spectra, line absorption spectra, and broad band absorption spectra similar to those exhibited by coloured organic substances. We have already mentioned that there seem now good prospects of proving that emission spectra are due to the vibrations of electrons within the atoms, and of calculating the positions of the lines from the vibrations of these electrons. Now these elements in gaseous form show very fine absorption bands or lines, and the positions of these lines, in the case of bromine, iodine, and sulphur, are identical with the positions of the lines in the emission spectra (Br.—Eder and Valenta, *Denkschr. Wien Acad.* 1899, *68*, 523–553; I.—Wüllner, *Pogg. Ann.* 1863, *120*, 158–167; Mitscherlich, *Pogg. Ann.* 1864, *121*, 459–488; Salet., *Compt. rend.*, 1872, *75*, 76–77; S.—Salet., *Compt. rend.* 1872, *74*, 865–866). Under other conditions, as in the liquid form or in solution, these elements show broad absorption bands. Wood (*Phil. Mag.* 1896, *41*, 423-431) has made the interesting observation that a solution of iodine in carbon bisulphide at the critical temperature shows fine lines identical in position and arrangement with those of iodine vapour. If the pressure be increased the absorption spectra of these elements in the gaseous form change from lines to broad bands. Hasselberg (*Mem. de l'Akad. de St. Petersb.* 1888 (7), *36*) and Konen (*Wied. Ann.* 1898, *65*, 285) have made interesting observations on the way in which the

lines are gradually converted into broad bands. The effect of increasing the pressure is to increase the intensity and width of the lines, and further to originate a general absorption which begins at the violet end of each band of lines, and, extending towards the red, finally becomes total.

It has been established that many of the fine black lines in the solar spectrum are due to absorption by the oxygen in the earth's atmosphere. The following are due to this cause, and therefore constitute the absorption spectrum of oxygen gas—

Group A.
The bands from 6960 to 6867 in Group B.
The greater number of the lines in Group *a*.
The Group 5840 to 5780 (a').
Group a''.

The Colours of the Simpler Compounds under Ordinary Conditions

The following investigators have pointed out relations between the colour of such compounds and their composition and the atomic weights of the constituent elements :—Ackroyd (*Chem. News*, 1876, *34*, 75–77); Flinders Petrie (*Nat.* 1876, *13*, 347–348); Carnelley (on the colour of chemical compounds chiefly as a function of the atomic weights of their constituent elements, *Phil. Mag.* 1884 (5), *18*, 130–140); Carnelley and Alexander (*Chem. News*, 1888, *57*, 217–218); Kastle (*Amer. Chem. Jour.* 1899, *21*, 398–413); and Bayley (*Chem. Soc. Trans.* 1880, *37*, 828–836).

Ackroyd gave the name "metachromatic scale" to the sequence of colours—white, violet, indigo, blue, green, yellow, orange, red, brown, black—being the colours assumed in succession by a dark body on being raised to white heat. According to Carnelley, in any series of compounds, A_xR_y, B_xR_y, C_xR_y . . . , where R is any element or group of elements, and A, B, C elements of the same group of Mendeleef's classification, the colour follows Ackroyd's scale as the atomic weight of A, B, C . . . increases.

Carey Lea (*Amer. Jour. of Sci.* 1895, *49*, 357 *et seq.*), from a consideration of the colours of their compounds, divided elements into (1) those with colourless ions; (2) transitional elements, the ions of which are coloured at some valencies and colourless at others; (3) elements whose ions are always coloured. For the purpose of determining which ions were coloured and which colourless he used the following criteria—

(1) When an electrolyte gives a solution in water which is colourless when dilute, both kation and anion are colourless.

(2) If an electrolyte gives a coloured dilute solution in water it is necessary first to consider the constitution of the anion. If this be a single atom, then the colour of the solution belongs entirely to the kation, for all elementary anions are colourless.

(3) Even if the anion is composite, information can often be gained. Many composite anions are colourless, *e.g.* SO_4. So that when sulphates give solutions that are coloured when dilute the colour must be due to the kation. The same is the case with nitrates, phosphates, carbonates, etc.

Having decided which elements are coloured and which colourless, he found that if all the elements are arranged in the order of their atomic weights the first eighteen are colourless, then follows a group of transitional and coloured elements, then nine colourless, then another group of transitional and coloured, then again nine colourless, another group of transitional and coloured, and finally, a group of six elements alternately colourless and coloured.

He came to the conclusion that the possession or non-possession of colour is a property of first-rate importance for the proper classification of the elements—that, in fact, the colourless elements should be considered by themselves and the coloured elements in another group by themselves. If the colourless elements are arranged in the order of their atomic weights they fall into nine natural groups, and if the coloured elements are considered by themselves in the same way they also fall into natural groups; and in this way the elements can be arranged in a periodic system which is

entirely free from the well-known defects of Mendeleef's classification. This new arrangement is as follows—

Elements with all colourless ions in numerical order forming nine natural groups

H.	F.	Cl.	Br	I	—
Li	Na	K	Rb	Cs	—
—	—	Ca	Sr	Ba	—
—	—	Sc	Y	La	—
Be	Mg	Zn	Cd	Hg	—
B	Al	Ga	In	—	—
C	Si	Ge	Sn	Pb	Th
N	P	As	Sb	—	—
O	S	Se	Te	—	—

Elements with ions always coloured. Also transitional elements in numerical order

[The symbols in heavy type denote transitional elements.]

Ti	Cr	**Cu**	**Nb**	Ru	**Ag**	**Ce**	Di	**Ta**	Os	**Tl**	U
V	Mn	—	**Mo**	Rh	—	—	Sm	**W**	Ir	**Bi**	—
—	Fe	—	—	Pd	—	—	Er	—	Pt	—	—
—	Co	—	—	—	—	—	—	—	Au	—	—
—	Ni	—	—	—	—	—	—	—	—	—	—

But it is unnecessary to propose an original classification of the elements in order to show that colour depends in a systematic way on atomic weight. If we take the elements in the usual periodic arrangement and study any series of simple compounds, such *e.g.* as the oxides, it is obvious that colour is developed in a regular way. In order to show this more clearly the following series of compounds have been considered—

(1) The normal oxides.

(2) The normal sulphides.

(3) The normal chlorides.

The normal oxide of the 1st group is understood to be of the type M_2O, of the 2nd group MO, of the 3rd group M_2O_3, and so on; similarly for the sulphides and chlorides.

The colours of these compounds have been tabulated, and in Plates I, II, and III these colours are shown at the positions occupied by the corresponding elements in the ordinary periodic tables. In those cases where the normal oxides, sulphides, or chlorides are unknown, the colour of the highest known oxide, sulphide, or chloride is given. Finally, in Plate IV the colours shown are those of the deepest coloured chlorides of the elements, irrespective of whether these happen to be normal, subnormal, or perchlorides. Nearly all elements give the deepest colour development when in the form of one of their chlorides,* although it is not always the normal chloride which shows the deepest colour. Plate IV thus gives us a very good idea of the deepest colours which the elements are capable of developing.

In order to avoid a patchy appearance the coloured areas have been made large enough for those corresponding to adjacent elements to meet.

Colours of the normal oxides (or highest oxides, when normal not known)

GROUP I.

Li_2O white	Na_2O white
K_2O „	Cu_2O red
Rb_2O „	Ag_2O black
Cs_2O „	Au_2O „

GROUP II.

BeO white	MgO white
CaO „	ZnO „
SrO „	CdO reddish brown
BaO „	HgO red

GROUP III.

B_2O_3 white	Al_2O_3 white
Sc_2O_3 „	Ga_2O_3 „
Y_2O_3 „	In_2O_3 pale yellow
La_2O_3 „	Tl_2O_3 dark red

* Iodides, chromates, etc., may have a deeper colour than any of the chlorides, but it seems natural to suppose that in these cases the negative radicle is partly responsible for the colour.

	I		II		III		IV		V		VI		VII		VIII		
1	H																
2	Li		Be		B		C		N		O		F				
3		Na		Mg		Al		Si		P		S		Cl			
4	K		Ca		Sc		Ti		V		Cr		M		Fe	Ni	Co
5		Cu		Zn		Ga		Ge		As		Se		Br			
6	Rb		Sr		Y		Zr		Nb		Mo				Rh	Ru	Pd
7		Ag		Cd		In		Sn		Sb		Te		I			
8	Cs		Ba		La		Ce		Di								
9																	
10									Ta		W				Os	Ir	Pt
11		Au		Hg		Tl		Pb		Bi							
12							Th				U						

KEY TO PLATES I–IV.

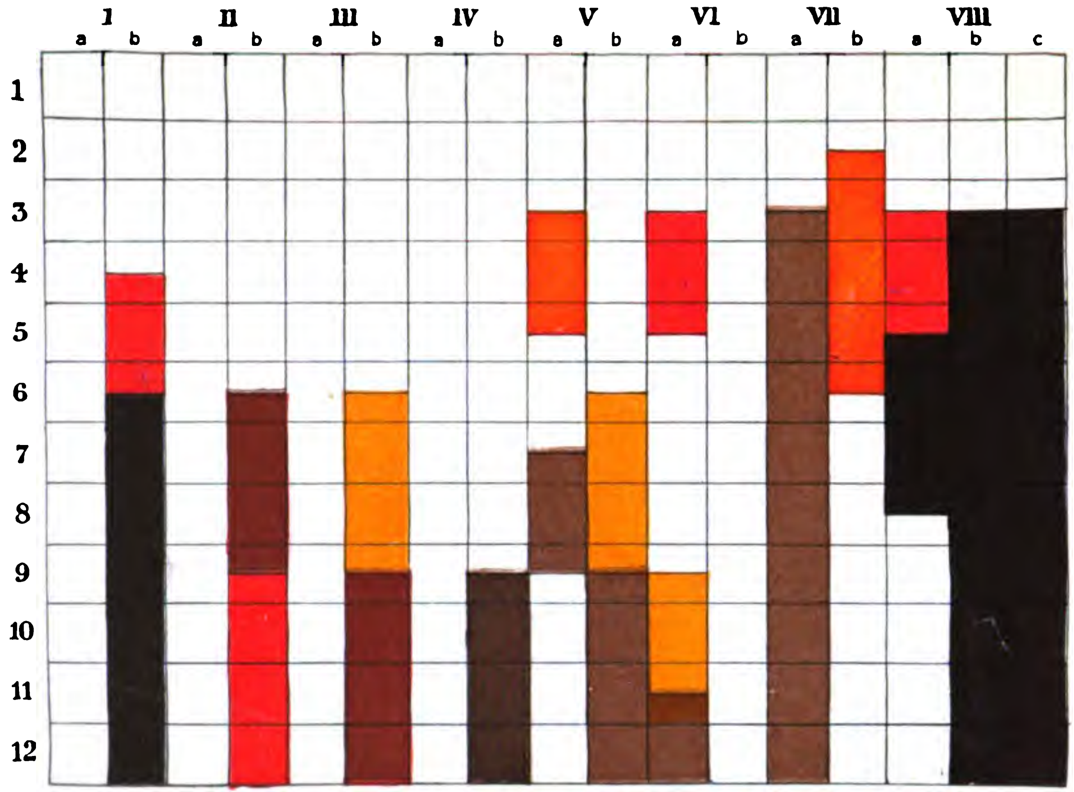


PLATE I.

Periodic arrangement showing colours of normal oxides (or highest oxide when normal not known).

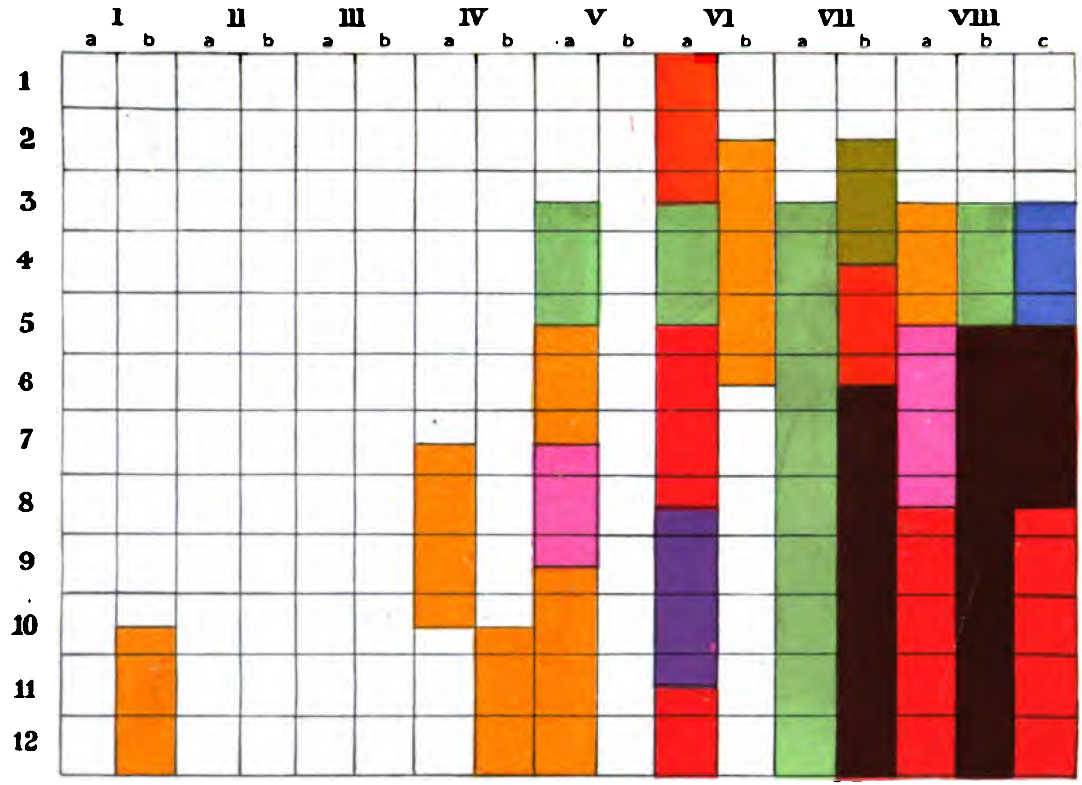


PLATE III.
Periodic arrangement showing colours of normal chlorides (or highest chloride when normal not known).

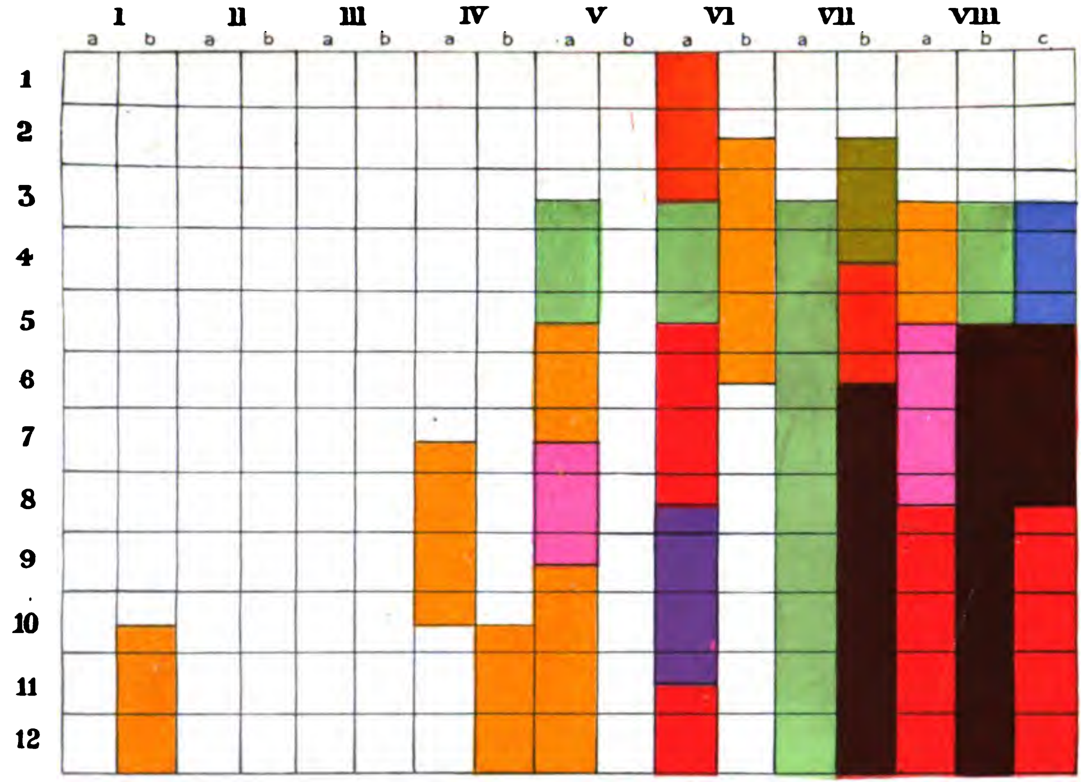


PLATE III.

Periodic arrangement showing colours of normal chlorides (or highest chloride when normal not known).

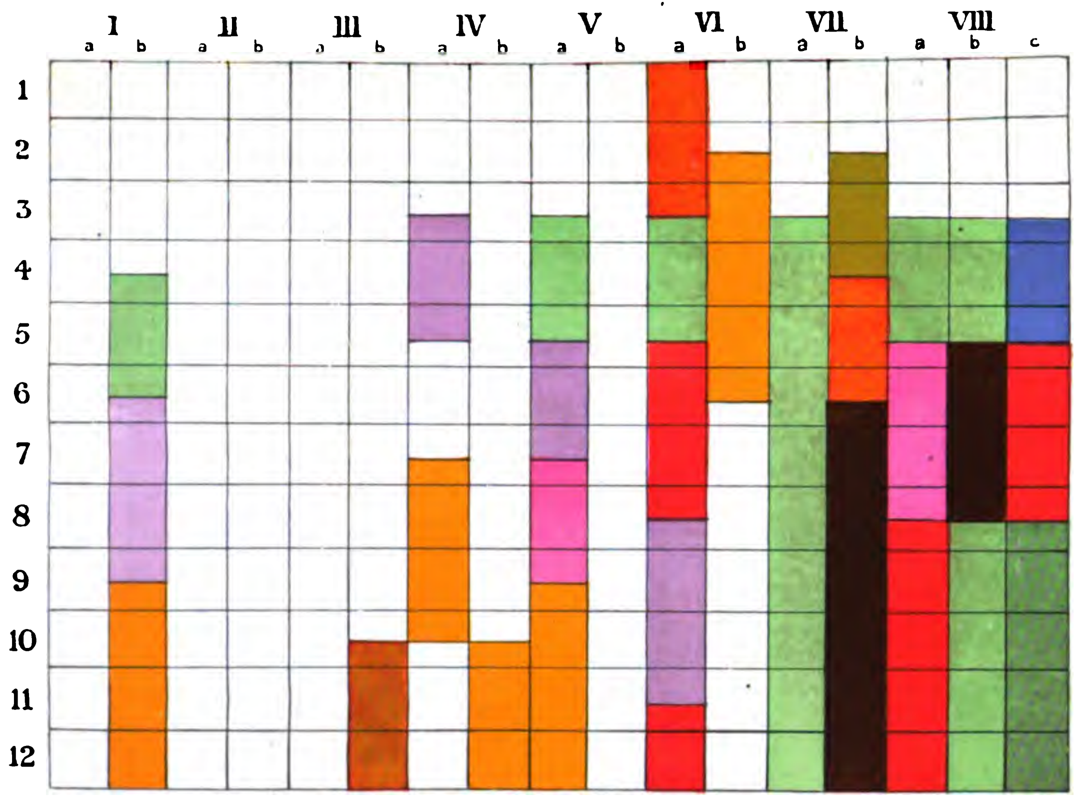


PLATE IV.
Periodic arrangement showing deepest colour exhibited by elements in form of chlorides.

GROUP IV.

CO_2 white	SiO_2 white
TiO_2 „	GeO_2 „
ZrO_2 „	SnO_2 „
CeO_2 „	PbO_2 brown
ThO_2 „	

GROUP V.

N_2O_5 white	P_2O_5 white
V_2O_5 yellowish red	As_2O_5 „
Nb_2O_5 white	Sb_2O_5 light yellow
Di_2O_5 brown	Bi_2O_5 brown
Ta_2O_5 white	

GROUP VI

[O_3 white (blue ?)]	SO_3 white
CrO_3 red	SeO_3 „
MoO_3 white	TeO_3 „
WO_3 yellow	
UO_3 brownish yellow	

GROUP VII.

F	[ClO_2 orange]
[MnO_2 brown]	Br
	[I_2O_5 white]

GROUP VIII.

[Fe_2O_3 red	Ni_2O_3 black,	Co_3O_4 black]
[RhO_2 grey	Ru_2O_3 blackish brown	PdO_2 black]
OsO_4 white	[IrO_2 black	PtO_2 black]

Colours of the normal sulphides (or highest sulphides when normal not known)

GROUP I.

Li_2S white	Na_2S white
K_2S „	Cu_2S black
Rb_2S „	Ag_2S brownish black
Cs_2S „	Au_2S „ „

Group II.

BeS white	MgS white
CaS „	ZnS „
SrS „	CdS yellow
BaS „	HgS red

Group III.

B_2S_3 yellowish (?)	Al_2S_3 yellow
ScS_3 ?	Ga_2S_3 ?
Y_2S_3 yellow	In_2S_3 yellow and brown
La_2S_3 „	Tl_2S_3 black

Group IV.

CS_2 white	SiS_2 white
TiS_2 yellow	GeS_2 „
ZrS_2 cinnamon brown	SnS_2 yellow
CeS_2 (or Ce_2S_3 ?) yellow	[PbS grey]
ThS_2 yellow	

Group V.

[NS orange red]	P_2S_5 yellow
V_2S_5 black	As_2S_5 „
Nb —	Sb_2S_5 yellowish red
[Di_2S_3 greenish brown]	[Bi_2S_3 blackish brown]
[Ta_2S_4 yellow]	

Group VI.

[O_2S_3 green ?]	[S_m yellow]
[Cr_2S_3 grey]	[SeS orange yellow]
MoS_3 reddish brown	TeS_3 blackish grey
WS_3 black	
[US_2 black]	

Group VII.

F —	[Cl_2S_2 yellow]
[MnS_2 reddish brown]	[Br_2S_2 red]
	[I_2S_2 dark grey]

Group VIII.

[FeS_2 yellow	NiS_2 grey	Co_3S_4 grey]
[Rh_2S_3 black	Ru_2S_3 ?	PdS_2 dark brown]
OsS_4 brown	[IrS_2 brown	PtS_2 grey]

Colours of normal chlorides (or highest chlorides when normal not known)

GROUP I.

LiCl white	NaCl white
KCl "	CuCl "
RbCl "	AgCl "
CsCl "	AuCl yellow

GROUP II.

$BeCl_2$ white	$MgCl_2$ white
$CaCl_2$ "	$ZnCl_2$ "
$SrCl_2$ "	$CdCl_2$ "
$BaCl_2$ "	$HgCl_2$ "

GROUP III.

BCl_3 white	$AlCl_3$ white
$ScCl_3$ "	$GaCl_3$ "
YCl_3 "	$InCl_3$ "
$LaCl_3$ "	$TlCl_3$ "

GROUP IV.

CCl_4 white	$SiCl_4$ white
$TiCl_4$ "	$GeCl_4$ "
$ZrCl_4$ "	$SnCl_4$ "
[$CeCl_3$ yellowish white]	$PbCl_4$ yellow
$ThCl_4$ white	

GROUP V.

N ?	PCl_5 white
[VCl_3 green]	[$AsCl_3$ "]
$NbCl_5$ yellow	$SbCl_5$ yellow?
[$DiCl_3$ rose red]	[$BiCl_3$ white]
$TaCl_5$ light yellow	

GROUP VI.

[O_2Cl orange]	[S_2Cl_2 yellow]
[$CrCl_3$ green]	[$SeCl_4$ light yellow]
[$MoCl_3$ copper red]	[$TeCl_4$ white]
WCl_6 dark violet	
[UCl_5 red]	

GROUP VII.

F —	[Cl_2 yellowish green]
[$MnCl_4$ green]	[BrCl reddish yellow]
	[ICl reddish brown]

GROUP VIII.

[$FeCl_3$ yellow	$NiCl_2$ green	$CoCl_2$ blue]
[$RhCl_3$ rose red	$RuCl_3$ dark brown	$PdCl_4$ brown]
[$OsCl_4$ red	$IrCl_4$ reddish black	$PtCl_4$ red]

Deepest-coloured chlorides (*when different from chloride in preceding table*)

GROUP I.

$CuCl_2$ green
Ag_2Cl violet

GROUP III.

$3TlCl, TlCl_3$ yellowish brown

GROUP IV.

$TiCl_3$ violet

GROUP V.

$NbCl_3$ violet black

GROUP VIII.

$FeCl_2$ green

$PdCl_2$ garnet red
$IrCl_3$ green, $PtCl_2$ greenish grey.

The following deductions may be made from an examination of the coloured plates—

(1) In any group of the periodic tables colour develops as the atomic weight increases. The sequence of colour development is yellow, red, brown, and black.

(2) In the first three groups more colour is developed in the odd than in the even series; in the 4th group the odd and even series show about the same amount of colour; whilst in the 5th, 6th, and 7th groups the even shows more than the odd series.

It follows from these two that neither the strongly positive nor the strongly negative elements show much colour development.

(3) Colour development reaches a maximum in the 8th group.

(4) In addition to—or, as it were, superposed upon—the preceding three tendencies we have an overpowering tendency for the development of deep colour in the middle of the first double period, *i.e.* in the elements V, Cr, Mn, Fe, Ni, Co, and Cu. The colour here is deep, as defined in Chapter I, *i.e.* violet, blue, and green appear.

The above four tendencies may be otherwise expressed by saying that (1) the elements in the middle of the long periods show selective absorption of the least refrangible rays of the visible spectrum; (2) increase of atomic weight causes increased general absorption, starting from the blue end of the spectrum and extending further and further towards the red.

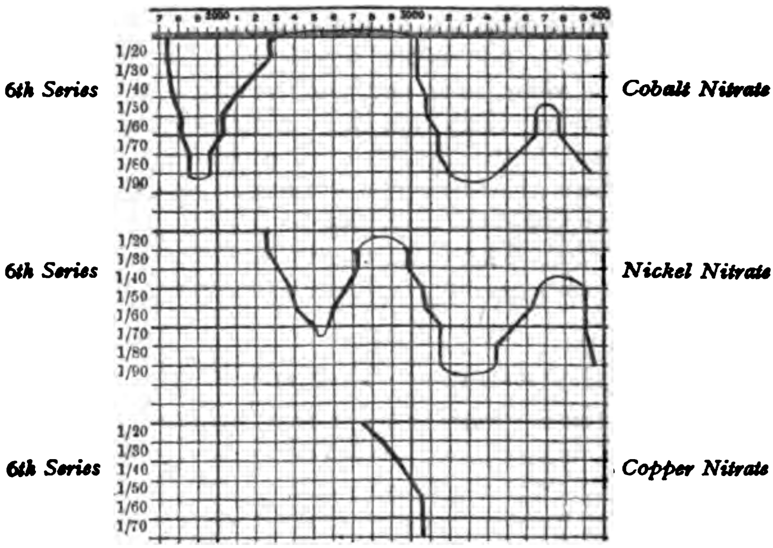
Absorption Spectra of Metallic Salts

The absorption spectra of solutions of the salts of chromium, manganese, iron, nickel, and cobalt have been examined by a large number of investigators. Most of their salts show a very limited number of rather broad bands, *e.g.* chromic chloride shows two bands at λ 7040–6850 and 6730–5380, cobalt chloride (anhydrous, blue) bands at λ 6300–5780 and λ 5410–5220, ferric chloride (in alcohol) three bands at 6800, 6200, and 5950, nickel salts show absorption at both ends of the visible spectrum and apparently a band at about 6600. Potassium permanganate shows about eight bands in the region from 5700–4400. Potassium chromate and bichromate show only general absorption at the blue end of the spectrum. Certain of the salts of the rare earths show a large number of very fine bands; the bands are so narrow that the solutions are scarcely coloured. Uranium salts also exhibit a considerable number of bands. Uranyl salts show about six bands, from λ 4900 to the blue end of the spectrum.

Fig. 65, showing the absorption curves of cobalt, nickel,

and copper nitrates, will serve to give an idea of the character of the absorption bands of strongly coloured inorganic salts.

Generally the salts formed from basic and acid radicles, which are both chromogenic, have the colour which one would expect to get from a co-operation of the two—in other words, the colour seems to be an additive property *e.g.* copper and chromium chromates are brown. But in some cases



Where the curved lines are thin the transmitted spectrum is feeble.

FIG 65.

(Reproduced from Hartley's paper, *Chem. Soc. Trans.*, 1903, 83, p. 224, bottom figure.)

there is an altogether unexpected colour development, as *e.g.* in the case of the ferro- and ferri- cyanides of iron, and also in the case of ferric thiocyanate.

Many of the metalammine salts are strongly and deeply coloured; *e.g.* the cobaltammines show most of the colours of the spectrum—yellow, orange, red, violet, green, and also brown. The complex ammonia salts of the platinum group of metals also show a considerable play of colours, including yellow, red, and green. There is here no very simple connection between constitution and colour, as may be seen by arranging

the cobaltammines in order according to chemical composition and noting the irregular display of colour.

$[Co(NH_3)_6]Cl'_3$	Luteo-salts	reddish yellow
$[Co(NH_3)_5Cl]Cl'_2$	Purpureo-salts	red
$[Co(NH_3)_4Cl_2]Cl' . H_2O$	Praseo-salts	emerald green
Ditto	(isomeric form)	violet
$[Co(NH_3)_4(NO_2)_2]_2SO_4$	Croceo-salts	orange yellow
$[Co(NH_3)_3(NO_2)_3]$	Erdmann's-salt	brownish green
$[Co(NH_3)_2(NO_2)_4]K$	—	yellow

According to Shibata (*J. Coll. Sci. Imp. Univ., Tokyo*, 1915, *37*, (2) 1–28) the cobaltammines show two or three maxima of absorption in the neighbourhood of the frequencies 2000, 3000, and 4000. The band at 2000 is exhibited by all the cobaltammines as well as by ordinary cobaltic salts, and he supposes that this band is due to the cobalt atom. The band at 3000 varies according to the nature of the groups with which the cobalt atom is associated, whilst that at 4000 is only exhibited by complex cobalt-compounds which contain the nitro-group.

Absorption Spectra of Simple Compounds in Gaseous Form

It has been shown that *water-vapour* in the earth's atmosphere is responsible for many of the fine dark lines observed in the solar spectrum. The following are due to this cause, and therefore constitute the absorption spectrum of water in gaseous form—

Group a (7450–7160).
The lines from 7164 to 6960 in Group B.
Group C (6600–6460).
Some of the lines of Group a (6350–6280).
The group at D (the rain-band) from 5970 to 5850.
Group δ (5780–5670).
Group ζ (5480–5420).
Group ι (5111–4981).

Nitrogen peroxide is specially interesting, as it is strongly coloured; and this colour is produced by a spectrum consisting of sharp lines, groups of sharp lines and broad bands.

The only useful measurements of the spectrum are given by Hasselberg (*Mem. Ac. St. Petersb.* 1878, (7) *26*, No. 4).

Iodine chloride has an absorption spectrum consisting of lines. Roscoe and Thorpe have measured 66 of these lines (*Phil. Trans.* 1876, *167*, 207–212).

Carbon bisulphide vapour shows a band in the ultra-violet, which Pauer has resolved into lines.

The fine lines in the absorption spectrum of *sulphur dioxide* have been already mentioned in Chapter VI, under the head of Baly's theory, according to which absorption bands in the visible and ultra-violet parts of the spectrum can be calculated from those in the infra-red. If only on account of this theory these fine line absorption spectra of simple compounds are of great interest, as it is possible that, on the one hand, the positions of their lines may be theoretically calculated, and, on the other hand, a relation may be shown between them and the absorption spectra of other substances which may be regarded as their derivatives: *e.g.* all hydroxy compounds may be regarded as derivatives of water; nitro- and nitroso-compounds may be regarded as derivatives of the oxides of nitrogen.

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